



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> <b>C08G 18/12, 18/48, 18/83</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/39179</b> <b>(43) International Publication Date:</b> 6 July 2000 (06.07.00)
<b>(21) International Application Number:</b> PCT/US99/31277 <b>(22) International Filing Date:</b> 30 December 1999 (30.12.99)  <b>(30) Priority Data:</b> 60/114,197 30 December 1998 (30.12.98) US 60/114,198 30 December 1998 (30.12.98) US 09/476,252 30 December 1999 (30.12.99) US  <b>(71) Applicant:</b> KIMBERLY-CLARK WORLDWIDE, INC. [US/US]; 401 N. Lake Street, Neenah, WI 54956 (US).  <b>(72) Inventors:</b> GREENE, Sharon, Linda; 235 Della Smith Lane, Canton, GA 30115-8137 (US). KAYLOR, Rosann, Marie; 7480 Williamsberg Drive, Cumming, GA 30131 (US). MORMAN, Michael, Todd; 555 Kings Peak, Alpharetta, GA 30201 (US).  <b>(74) Agents:</b> FLACK, Steven, D. et al.; Kimberly-Clark Worldwide, Inc., 401 N. Lake Street, Neenah, WI 54956 (US).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> SUPERABSORBENT AND ELASTIC POLYMERIC MATERIAL INCLUDING POLYETHYLENE GLYCOL AND POLY-TETRAMETHYLENE ETHER GLYCOL SOFT SEGMENTS AND METHODS OF MAKING SAME		
<b>(57) Abstract</b>  A superabsorbent and elastomeric thermoplastic polymer includes soft segments and hard segments which contribute to the functionality of the polymer. The soft segments have a molecular weight in the range from about 600 to about 20,000 and are selected from the group of PEG, PEO, PTMEG, PPG and PPO. The hard segments are selected from the group of polyurethanes, polyamides, polyesters, polyureas, and combinations thereof. The soft and hard segments are covalently bound together by means of urethane, amide, ester or secondary urea linkages or combinations.		

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SUPERABSORBENT AND ELASTIC POLYMERIC MATERIAL INCLUDING POLYETHYLENE GLYCOL AND POLY-TETRAMETHYLENE ETHER GLYCOL SOFT SEGMENTS AND METHODS OF MAKING SAME

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**Field of the Invention**

The present invention relates to superabsorbent and elastic materials. More particularly, the present invention relates to a single polymeric material which possesses both attributes of superabsorbency and elasticity, which can be formed into fibers, films, foams, or injection-molded articles, and which is particularly suitable for use in personal care products that require a stretchable absorbent member such as diapers, sanitary products, absorbent feminine hygiene related products and health care products such as wound care products (e.g. bandages), delivery systems (e.g. transdermal), and implants.

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**Background of the Invention**

The use of disposable personal care products for body fluid management, such as diapers, sanitary products, incontinent pads, and the like have gained wide acceptance by consumers. Furthermore, the use of wrap bandages, such as Ace™ and other flexible bandages, and transdermal delivery systems, have become common methods for treating limb injuries and other ailments, addictions and diseases.

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Such personal care products are typically comprised of a batt or absorbent portion which is wrapped within a liner. The batt typically functions to absorb body fluids. The batt may be comprised of cellulose fibers which allows for absorption of body fluids between the fibers. The liner usually is a nonwoven web or perforated film of a polyolefin such as polyethylene or polypropylene.

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Such bandages typically include an elastic layer to provide a conforming fit over an injury, to protect the wound from the surrounding environment, and which may also allow for absorption of body fluids from a wound, between absorbent fibers of the bandage.

Transdermal delivery systems typically allow a medical preparation, pharmaceutical, or hydration preparation to be impregnated in a substrate which is wrapped or placed adjacent to the skin. The substrate utilized in the system must be sufficiently absorbent to retain the medicament, pharmaceutical or water, but which will also allow these materials to pass in a controlled manner from the substrate to a wound, or across the skin layer into the body of the patients /or treated individuals.

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Significant efforts have been made to make such disposable absorbent products and bandages more efficient, comfortable and form fitting for the consumer. The ability of a

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personal care product to remove and keep body fluids separated from the skin has been perceived as a desirable attribute and is believed to be a factor in the reduction of such skin problems as diaper rash. Therefore, much of the research efforts have focused on increasing the absorbent capacity of the product and/or increasing the wetting rate of the product, while at the same time increasing the ability of the product to retain absorbed fluid

and including a conforming fit. To this end, increased absorbent capacity or fluid retention typically has been accomplished in personal care products by incorporating a superabsorbent material (SAM) into the batt. Superabsorbent materials, also referred to as hydrogels, frequently are based on acrylate and methacrylate polymers and copolymers. Superabsorbent materials typically absorb water molecules into their polymer matrix. Other hydrogels are based on starch or a modified starch. Hydrogels prepared from hydrolyzed crosslinked polyacrylamides, crosslinked sulfonated polystyrenes, or those based on maleic anhydride have also been described.

The superabsorbent material is often incorporated into batts in particulate form. Unfortunately, particulate superabsorbents often migrate in, or fall out of the absorbent product. The superabsorbents then end up on a user's skin, which is disfavored by consumers. Furthermore, the superabsorbents may exhibit gel-blocking, especially if uniform distribution is lost. Gel-blocking is the phenomenon which prevents the migration of fluid. Essentially, the superabsorbent particles block the migration of fluid by accumulating in large aggregates. Moreover, the use of particulate superabsorbents complicates the manufacturing process. The particulate nature of the superabsorbents also limits applications for the superabsorbents. Superabsorbent particles have also been used within meltblown webs, as described in U.S. Patent 4,429,001 to Kolpin et al. However, when such webs are combined with elastic materials, the superabsorbent materials often lock up or restrict elongation/retraction of the elastic materials when the superabsorbent materials have incorporated water molecules.

As an alternative approach to increasing absorbency capacity, paper/pulp content has been increased within consumer care products. The increase in pulp fiber, while having a direct impact on the level of absorbency, does not provide for an increase in elasticity of the overall product. Furthermore, the increase in pulp content can lead to an increase in bulk of the personal care product.

It has also been known that melt processable (thermoplastic) superabsorbent material can be based on linear polyether urethanes, consisting of polyethylene glycol (PEG) soft segments for absorbency. This superabsorbent material can be extruded into fibers for incorporation into nonwoven webs. Such are described in U.S. Patents 4,767,825 and 4,820,577 to Pazos et al., and Morman et al. respectively, and which are hereby

incorporated by reference in their entirety. The polyethylene glycol soft segments of these superabsorbents are made water insoluble by using a minimum amount of physical cross-links formed from hard segments (polyurethanes, polyesters or polyamides). However, this material has not demonstrated significant elasticity, and at high PEG block molecular weight levels is glassy and brittle. While such materials may be capable of being processed into films or nonwoven webs, they must be used in combination with separate elastic components in order to produce a product which demonstrates both elasticity and superabsorbency.

At the same time that efforts have been under way to increase a product's absorbency, efforts have also focused on making the products more comfortable to wear. In this regard, product components have been made to stretch or give at specific points, such as in the waist area and around leg openings. In order to provide stretch in these areas, elastic components have been strategically incorporated into both personal care and health care products. Such components include strips or strands of elastomeric materials such as Lycra™ or Kraton™-based materials which are positioned at limited locations in the product. Such components are often costly, and consequently, they cannot be used liberally to increase body conformance uniformly throughout the product. Furthermore, it has proven difficult to place such elastic materials in such areas as body creases or recesses, without adding significant costs to the consumer.

Various types of materials and material arrangements have been proposed for use in personal care products to simultaneously increase both absorbency and body conformance. In particular, efforts have focused on improving the absorbency and elasticity of personal care products in areas of the products which contact or are disposed over body creases, or which function to provide the tight fit of the products to the body, e.g. leg openings.

Typically, a greater amount of absorbent material is placed in areas of the personal care product most likely to be in contact with body fluids. In contrast, little or no absorbent material is placed in the other areas, such as around the leg openings and waist openings, in the case of a diaper.

In particular, to deliver personal care products with absorbency and elasticity, separate superabsorbent and elastic materials have been used in constructions, such as that described in U. S. Patent Nos. 5,662,634 to Yamamoto et al. and 5,451,219 to Susuki et al. However, such constructions are typically very complex. The constructions often rely on separate wettable fibers and elastomeric fibers. This two material construction approach, while effective for providing stretch and absorbency, often poses a manufacturing challenge.

The two material construction would tend not to retract from the stretch as the wettable

fibers do not retract but inhibit the elastic fibers. Furthermore, the two material construction approach adds additional costs and steps to the manufacturing process.

Finally, the company Elf Atochem has marketed breathable films under the brand name PEBAX®. Such materials include polyether block amides having polyamide rigid or  
5 hard segments and polyether soft segments. The structure of the PEBAX materials consists of a regular linear chain of rigid polyamide segments interspaced with flexible polyether segments. These extrudable resins for use in films, have elastic memory and some grades are hydrophilic. The resulting films are considered waterproof and breathable. In particular, the 33 series and 62 series of materials offer very low water absorption of 1.2 % and 3.5 %  
10 for 24 hours in water, based on the ASTM D570 test, while the 4011 grade resins are considered more hydrophilic. However, Elf Atochem's literature describes highly absorbent material as 120 % absorption for 24 hours in water, i.e. 1.2 grams of water per gram of polymer. The elasticity measurements of these resins also vary according to percentage of polyether content.

15 Finally, it is known that thermally reversible urethane chemistry can be used to create separate polymers which either demonstrate elasticity or superabsorbency. For instance, thermally reversible chemistry has been described in U.S. Patent Nos. 5,047,456, 5,219,974 and 5,491,210 each to Onwumere et al., each being incorporated by reference in its entirety. However, the polymers do not demonstrate both attributes of  
20 elasticity and absorbency.

It would therefore be desirable to have a stretchable and superabsorbent personal care product of simple construction. While current technology in this area allows for stretchable outer covers and liners, it has been a challenge to make these portions of personal care products absorbent as well. While stretchable absorbent products have been  
25 described in the literature, e.g. U.S. Patent 5,645,542 to Anjur et al., it would still be desirable to have one material that stretches, recovers and is also a superabsorbent.

Therefore it is seen that a need still exists for a single material which demonstrates both elasticity and superabsorbency functionality. A need exists for a superabsorbent and elastic material which demonstrates multidirectional stretch. A need also exists for a  
30 superabsorbent and elastic material which is melt-processable. Further, a need exists for a superabsorbent and elastic material which may be synthesized in solution. Further, a need exists for a single material which does not require containment of its superabsorbent elements as is required for hydrogel particulate materials. Furthermore, a need still exists for a single material which exhibits elasticity sufficient for it to conform to the human form,  
35 while providing superabsorbency. A need also exists for a single material which exhibits sufficient superabsorbency to retain moisture and yet allows sufficient body conformance for

areas such as the waist or leg/cuff regions, i.e. to prevent leakage at these areas. Finally, a need still exists for a single material which exhibits the dual functionality of superabsorbency and elasticity and which can be made into films, fibers, nonwoven webs, foams and injection molded products. It is to such needs that the present invention is directed.

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### Summary of the Invention

The present invention meets the needs of the art by providing a single superabsorbent and elastic polymeric composition which can be melt processable into fibers, films, foams and injection molded articles. It has now been discovered that certain polymeric  
10 compositions containing polyalkoxy groups, such as polyethylene glycol (PEG) and polytetramethylene ether glycol (PTMEG) soft segments, exhibit superabsorbency and/or elasticity dual functionality. Such single compositions may be made into films, fibers, foams, webs, and injection-molded products, making the compositions particularly suited for use in personal care products and bandage applications.

15 Accordingly, the present invention provides a superabsorbent and elastomeric thermoplastic polymer comprising PEG and PTMEG soft segment components each having a molecular weight in the range from about 600 to about 20,000, and hard segments selected from the group consisting of polyurethanes, polyamides, polyesters, polyureas, and combinations thereof; wherein the soft and hard segments are covalently bound together by  
20 means of urethane, amide, ester or secondary urea linkages or combinations thereof.

The present invention also provides a nonwoven web comprising fibers composed of a superabsorbent and elastomeric thermoplastic polymer comprising PEG and PTMEG soft segment components each having a molecular weight in the range from about 600 to about 20,000; and hard segments selected from the group consisting of polyurethanes,  
25 polyamides, polyesters, polyureas, and combinations thereof wherein the soft and hard segments are covalently bound together by means of urethane, amide, ester or secondary urea linkages or combinations thereof.

The present invention also provides a melt processable superabsorbent, elastomeric polymer comprising PEG and PTMEG soft segment components each having a molecular  
30 weight in the range from about 600 to about 20,000 and hard segments selected from the group consisting of polyurethanes, polyamides, polyesters, and combinations thereof wherein the soft and hard segments are covalently bound together by means of urethane, amide, or ester linkages or combinations thereof.

The present invention also comprises a method of making a superabsorbent  
35 elastomeric thermoplastic polymer which comprises a) combining a sample of PEG with a sample of PTMEG, b) drying the samples, c) adding a diisocyanate to the PEG/PTMEG

combination in an equivalent mole ratio for endcapping or coupling the PEG and PTMEG samples, d) heating and stirring the combination, and then e) adding additional diisocyanate and a diol to the combination while stirring.

5 In a further alternate embodiment, the present invention provides a superabsorbent and elastomeric thermoplastic polymer comprising a) PEG, PTMEG and PPG soft segment components each having a molecular weight in the range from about 600 to about 20,000 ; and b) hard segments selected from the group consisting of polyurethanes, polyamides, polyesters, polyureas, and combinations thereof wherein the soft and hard segments are covalently bound together by means of urethane, amide, ester or secondary urea linkages  
10 or combinations thereof.

The present invention also provides a nonwoven web comprising fibers composed of a superabsorbent and elastomeric thermoplastic polymer comprising a) PEG, PTMEG and PPG soft segment components each having a molecular weight in the range from about 600 to about 20,000; and hard segments selected from the group consisting of polyurethanes,  
15 polyamides, polyesters, polyureas, and combinations thereof wherein the soft and hard segments are covalently bound together by means of urethane, amide, ester or secondary urea linkages or combinations thereof.

The present invention also provides a melt processable superabsorbent, elastomeric polymer comprising a) PEG, PTMEG and PPG soft segment components each having a  
20 molecular weight in the range from about 600 to about 20,000 ; and hard segments selected from the group consisting of polyurethanes, polyamides, polyesters, and combinations thereof; wherein the soft and hard segments are covalently bound together by means of urethane, amide, or ester linkages or combinations thereof.

The present invention also comprises a method of making a superabsorbent elastomeric thermoplastic polymer which comprises a) combining a sample of PEG with a sample of PTMEG and PPG, b) drying the samples, c) adding a diisocyanate to the PEG/PTMEG/PPG combination in an equivalent mole ratio for endcapping or coupling the PEG, PTMEG, and PPG samples, d) heating and stirring the combination, and e) adding additional diisocyanate and a diol to the combination while stirring.  
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30 Finally, in another alternate embodiment certain polyurethane compositions containing both polyethylene glycol (PEG) and polytetramethylene ether glycol (PTMEG) soft segments exhibit superabsorbency and elasticity dual functionality and are thermally-processable in part because of reversible degradation of covalent cross-links within the polymer. During processing, the polymer is heated to temperatures high enough to cause  
35 reversible degradation of the covalent links. After processing, and upon cooling, the



crosslinks reform to provide increased strength, reduced solubility, improved elastic properties and other material properties.

In particular, the present invention also provides a superabsorbent and elastomeric thermoplastic polymer comprising a) PEG and PTMEG soft segment components each having a molecular weight in the range from about 600 to about 20,000 ; and b) hard segments selected from the group consisting of polyurethanes, polyamides, polyesters, polyureas, and combinations thereof; wherein the soft and hard segments are covalently bound together by means of urethane, amide, ester or secondary urea linkages or combinations thereof and wherein the hard segments include aromatic diisocyanate and aromatic diol portions.

The present invention also provides a nonwoven web comprising fibers composed of a superabsorbent and elastomeric thermoplastic polymer comprising a) PEG and PTMEG soft segment components each having a molecular weight in the range from about 600 to about 20,000; and b) hard segments selected from the group consisting of polyurethanes, polyamides, polyesters, polyureas, and combinations thereof; wherein the soft and hard segments are covalently bound together by means of urethane, amide, ester or secondary urea linkages or combinations thereof and wherein the hard segments include aromatic diisocyanate and aromatic diol portions.

The present invention also provides a melt processable superabsorbent, elastomeric polymer comprising a) PEG and PTMEG soft segment components each having a molecular weight in the range from about 600 to about 20,000 ; and b) hard segments selected from the group consisting of polyurethanes, polyamides, polyesters, and combinations thereof; wherein the soft and hard segments are covalently bound together by means of urethane, amide, ester linkages or combinations thereof and wherein the hard segment includes aromatic diisocyanate and aromatic diol portions.

Alternatively, low molecular weight PEGs having a molecular weight of less than or equal to 600, may be used in combination with PTMEG in the inventive polymers. Additionally, being that low molecular weight PEGs can serve as both absorbent and elastic soft segments, they may be used without PTMEG in inventive polymers which include aromatic diisocyanate/ aromatic diol portions in the hard segments.

The present invention also comprises a method of making a superabsorbent elastomeric polymer which comprises a) combining a sample of PEG with a sample of PTMEG, b) drying the samples, c) adding an aromatic and optionally a nonaromatic isocyanate to the samples up to an equivalent mole ratio for endcapping or coupling PEG and PTMEG, d) heating and stirring the samples, and e) adding additional aromatic diisocyanate and an aromatic diol to the sample while stirring.

Furthermore, the present invention also comprises a method of making a functionally crosslinked superabsorbent elastomeric polymer which comprises a) combining a sample of PEG with a sample of PTMEG in a suitable container, b) drying the samples, c) adding a trifunctional reagent such as a tri-isocyanate or diisocyanate to the container in an equivalent amount to the mole total of PEG and PTMEG, d) heating and stirring the sample, e) adding additional trifunctional reagent such as tri-isocyanate or diisocyanate and triol and/or diol to the sample while stirring.

Other objects, features and advantages of the present invention will become apparent upon reading the following detailed description of the disclosed embodiments of the present invention, in conjunction with the appended drawings and claims.

### **Brief Description of the Drawings**

FIGS. 1 and 2 are graphs illustrating the Force in grams versus Percent Elongation when a sample is cycled once to 65% elongation and then taken to break.

FIGS. 3 and 4 are graphs illustrating the Force in grams versus Percent Elongation when a sample is cycled once to 117% elongation and then taken to break.

FIGS. 5 and 6 are graphs illustrating the Force in grams versus Percent Elongation when a sample is cycled once to 307% elongation and then taken to break.

FIG. 7 is a perspective schematic view illustrating one embodiment of a process for forming a meltblown nonwoven web of superabsorbent and elastic polymer made in accordance with the present invention.

FIG. 8 is a perspective view of the meltblowing die shown in FIG. 7 which illustrates the linear arrangement of the capillaries of the die.

FIG. 9 is a generalized flow diagram illustrating one embodiment of a process for forming a spunbond nonwoven web of a superabsorbent and elastic polymer made in accordance with the present invention.

FIG. 10 is a perspective schematic view illustrating a second embodiment of a process for forming a spunbond nonwoven web of a superabsorbent and elastic polymer made in accordance with the present invention.

FIG. 11 is a perspective schematic view illustrating one embodiment of a process for forming a film of a superabsorbent and elastic polymer made in accordance with the present invention and a laminate including such film.

FIG. 12 is a cross sectional view of a film laminate made according to the process of FIG. 11.

### Detailed Description of the Invention

#### Definitions

As used herein the term **"nonwoven fabric or web"** means a web having a structure of individual fibers or threads which are interlaid, but not in an identifiable manner as in a knitted fabric. Nonwoven fabrics or webs have been formed from many processes such as for example, meltblowing processes, spunbonding processes, and bonded carded web processes. The basis weight of nonwoven fabrics is usually expressed in ounces of material per square yard (osy) or grams per square meter (gsm) and the fiber diameters useful are usually expressed in microns. (Note that to convert from osy to gsm, multiply osy by 33.91).

As used herein the term **"nonwoven material"** shall mean nonwoven fabric or webs, film scrim and foam.

As used herein the term **"modulus"** is the property of a material representative of deformation. It is the ratio of stress to strain for a material under a given loading condition.

As used herein the term **"% Elongation"** is the ratio of the extension of material to the length of the material prior to testing.

As used herein the term **"composite elastic material"** refers to an elastic material which may be a multicomponent material or a multilayer material in which one layer is elastic. These materials may be, for example, **"stretch bonded"** laminates and **"neck bonded"** laminates.

Conventionally, **"stretch bonded"** refers to an elastic member being bonded to another member while the elastic member is extended at least about 25 percent of its relaxed length. **"Stretch bonded laminate"** refers to a composite material having at least two layers in which one layer is a gatherable layer and the other layer is an elastic layer. The layers are joined together when the elastic layer is in an extended condition so that upon relaxing the layers, the gatherable layer is gathered. Such a multilayer composite elastic material may be stretched to the extent that the nonelastic material gathered between the bond locations allows the elastic material to elongate. One type of stretch

bonded laminate is disclosed, for example, by U.S. Patent 4,720,415 to Vander Wielen et al., hereby incorporated by reference in its entirety, in which multiple layers of the same elastomeric polymer produced from multiple banks of extruders are used. Other composite elastic materials are disclosed in U.S. Patent 4,789,699 to Kieffer et al., U.S. Patent 5 4,781,966 to Taylor and U.S. Patents 4,657,802 and 4,652,487 to Morman and 4,655,760 to Morman et al, each of the patents being hereby incorporated by reference in its entirety.

Conventionally, "**neck bonded**" refers to an elastic member being bonded to a non-elastic member while the non-elastic member is extended in one direction to be necked in a perpendicular direction. "**Neck bonded laminate**" refers to a composite material having 10 at least two layers in which one layer is a necked, non-elastic layer and the other layer is an elastic layer. The layers are joined together when the non-elastic layer is in a necked condition. Examples of neck-bonded laminates are such as those described in U.S. Patents 5,226,992, 4,981,747, 4,965,122 and 5,336,545 to Morman incorporated herein by reference in their entirety.

15 As used herein the term "**spunbond**" fibers refers to small diameter fibers which are formed by extruding molten thermoplastic material as filaments from a plurality of fine, usually circular capillaries of a spinneret with the diameter of the extruded filaments then being rapidly reduced as by, for example, in U.S. Patent 4,340,563 to Appel et al., and U.S. Patent 3,692,618 to Dorschner et al., U.S. Patent 3,802,817 to Matsuki et al., U.S. Patents 20 3,338,992 and 3,341,394 to Kinney, U.S. Patent 3,502,763 to Hartman, and U.S. Patent 3,542,615 to Dobo et al. each being hereby incorporated by reference in its entirety. Spunbond fibers are generally not tacky when they are deposited onto a collecting surface. Spunbond fibers are generally continuous and have average diameters (from a sample of at least 10) larger than 7 microns, more particularly, between about 10 and 40 microns.

25 As used herein the term "**meltblown**" fibers means fibers formed by extruding a molten thermoplastic material through a plurality of fine, usually circular, die capillaries as molten threads or filaments into converging high velocity, usually hot, gas (e.g. air) streams which attenuate the filaments of molten thermoplastic material to reduce their diameter, which may be to microfiber diameter. Thereafter, the meltblown fibers are carried by the 30 high velocity gas stream and are deposited on a collecting surface to form a web of randomly disbursed meltblown fibers. Such a process is disclosed, for example, in U.S. Patent 3,849,241 to Butin et al. hereby incorporated by reference in its entirety. Meltblown fibers are microfibers which may be continuous or discontinuous, and are generally smaller than 10 microns in average diameter.

35 As used herein "**multilayer laminate**" means a laminate wherein some of the layers are either spunbond or meltblown such as a spunbond/meltblown/spunbond (SMS) laminate

and others as disclosed in U.S. Patent 4,041,203 to Brock et al., U.S. Patent 5,169,706 to Collier, et al, U.S. Patent 5,145,727 to Potts et al., U.S. Patent 5,178,931 to Perkins et al. and U.S. Patent 5,188,885 to Timmons et al. each being incorporated by reference in its entirety. Such a laminate may be made by sequentially depositing onto a moving forming belt first a spunbond fabric layer, then a meltblown fabric layer and last another spunbond layer and then bonding the laminate by any one of various bonding methods, such as thermal point bonding or adhesive bonding. Alternatively, the fabric layers may be made individually, collected in rolls, and combined in a separate bonding step. Such fabrics usually have a basis weight of from about 0.1 to 12 osy, or more particularly from about 0.75 to about 3 osy. Multilayer laminates may also have various numbers of meltblown layers or multiple spunbond layers in many different configurations and may include other materials like films (F), bonded carded webs (BCW), or coform materials, e.g. SMMS, SM, SFS, etc.

As used herein, the term "**coform**" means a process in which at least one meltblown diehead is arranged near a chute through which other materials are added to the web while it is forming. Such other materials may be pulp, superabsorbent particles, cellulose or staple fibers, for example. Corform processes are shown in commonly assigned U.S. Patents 4,818,464 to Lau and 4,100,324 to Anderson et al. each incorporated by reference in their entirety.

As used herein, the term "**polymer**" includes copolymers, such as for example, block, graft, random and alternating copolymers and blends and modifications thereof. Unless otherwise specifically limited, the term "**polymer**" shall include all possible geometrical configurations of the molecule. These configurations include, but are not limited to isotactic, syndiotactic and random symmetries.

As used herein, the term "**personal care product**" means diapers, swimwear, training pants, absorbent underpants, adult incontinence products, and feminine hygiene products.

As used herein the term "**health care product**" means bandages, delivery systems such as transdermal delivery systems, and implants.

As used herein the terms "**superabsorbent**" or "**superabsorbent material**" refers to a water-swellaable, water-soluble organic or inorganic material that has been made insoluble to water and is capable, under favorable conditions, of absorbing at least about 2 times its weight. An example of favorable conditions can be those conditions of ASTM test D570. While there are many methods to measure absorbency, the values provided herein are based on free swell values unless otherwise stated. Absorption of the water molecules occurs within the polymer matrix of the superabsorbent as opposed to absorption within a

fibrous matrix. For the purposes of this application the superabsorbency of a material is calculated in accordance with the following equation, unless otherwise noted:

$$\text{superabsorbency} = \frac{\text{Weight of Polymer Plus Water} - \text{Initial Weight of Polymer}}{\text{Initial Weight of Polymer}}$$

The percent water is calculated in accordance with the following equation:

$$\frac{\text{Weight of water}}{(\text{Weight of dry Polymer} + \text{Weight of Water})} \times 100$$

As used herein the terms “**absorbent**” and “**absorbent material**” refer to a material capable, under favorable conditions, of absorbing water/saline solution within its fibrous interstices as opposed to within a polymeric matrix. It should be understood that under this definition, it is possible for a composite material to demonstrate concurrently both absorbency as well as superabsorbency. In general, absorbency can occur very rapidly when a nonwoven is submersed in a liquid while superabsorbency takes a longer time, as the liquid has to diffuse into the polymer.

As used herein the terms “**elastic**” and “**elastomeric**” refer to a material which, upon application of a biasing force, is extensible or elongatable in at least one direction and which demonstrates recovery upon release of the biasing force within 1-2 seconds of release. For purposes of the present invention an elastomeric material has the capability of being stretched to an elongation of at least about 25% of its original relaxed length, i.e. can be stretched to at least 1.25 times its original relaxed length, and will upon release of the stretching force recover within 1-2 seconds at least about 30% of the elongation, i.e. will in the case of 25% elongation, contract to an elongation of not more than about 1.175 times its original relaxed length or 17.5%.

As used herein, the term “**Percent Permanent Set**” is the permanent deformation after an elongation divided by the length of the elongation times 100.

As used herein, the term “**inelastic**” or “**nonelastic**” refers to any material which does not fall within the definition of “**elastic**” above.

The superabsorbent and elastomeric thermoplastic composition of the present invention comprises soft segments and hard segments, each of these segments being described herein in terms of segment constituents or composition and by general formula.

As used herein, the term “**soft segment**” of the polymeric chain refers to those portions of the polymeric composition which contribute to the absorbency and elasticity of the polymer.

The term "**soft segment**" also refers to the initial molecular weight of each of the elastic and absorbent units in a polymer chain, e.g. soft segments containing polyalkoxy groups such as polyethylene glycol (PEG) and/or (PEO) and/or polytetramethylene ether glycol (PTMEG) and polypropylene glycol (PPG) and/or (PPO), in addition to the same number of equivalents of methylene diphenyl diisocyanate (MDI) or other diisocyanate which may be used in the polymerization reaction. As an example, when the phrase "PEG and PTMEG soft segments having a molecular weight in the range from about 600 to 20,000" is used, the phrase should be interpreted to mean each of the individual PEG and PTMEG soft segment units have a molecular weight in the stated range.

For the purposes of this application it should be recognized that the term polyethylene glycol encompasses the term poly(oxyethylene) and is represented generally by the following structural formula:  $\text{HOCH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OH}$  or  $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ . Polyethylene glycol is derived by a condensation reaction of ethylene glycol or of ethylene oxide and water.

For the purposes of this application, reference to the PPG molecule should also encompass the PPO molecule.

As used herein the "**hard segment**" of the polymeric chain must be essentially insoluble in water and must phase separate from the soft segment. The hard segment is selected from the group consisting of polyurethanes, polyamides, polyesters, polyureas, and combinations thereof, although if polyureas are utilized, the final compositions are less melt processable than if one of the other hard segments were to be used. This is possibly due to thermal degradation which occurs from the high heat required during the polymerization reactions including polyureas.

The hard segment of the polymer consists of functional groups which provide insolubility for the absorbent components as well as the anchors for the elastic components. Examples of such include the resulting crystalline regions formed by the reaction of a chain extender such as a short chain diol (e.g. butane diol) with a diisocyanate. Specific examples of such hard segments include the urethane formed from the reaction of methylenediphenyldiisocyanate (MDI) and butanediol (BDO). Another example includes the resulting crystalline regions formed by the reaction of a chain extender such as an aromatic diol with an aromatic isocyanate.

As used herein the term "**hard segment**" may also refer to the weight of the remaining non-soft segment units in the polymer chain, e.g. the diisocyanate remaining after the weight of the PEG, PTMEG, and PPG and equivalents of diisocyanate are considered.

As used herein, the term "**uniform**" shall mean dispersed over the entire composition, fiber, film or material rather than concentrated in discrete areas.

As used herein, the term "**endcapped**" shall refer to an addition reaction in which the end groups/tails of a soft segment reactant are replaced with another functional group such as a diisocyanate.

5 As used herein the terms "**chain extension**," "**extension**," and "**chain extension reaction**" shall refer to an addition reaction which allows a polymer chain to be lengthened.

As used herein the term "**chain extender**" shall refer to the chemical reactant which allows for a chain extension.

10 As used herein, the term "**machine direction**" or "**MD**" means the length of a fabric in the direction in which it is produced. The terms "**cross machine direction**," "**cross directional**," or "**CD**" mean the width of fabric, i.e. a direction generally perpendicular to the MD.

15 It has been found that films (nonporous or porous), and fibers demonstrating varying characteristics including but not limited to, superabsorbency and elasticity can be prepared by varying the ratio of hard and soft segments in a polymer, by varying the ratio of soft segment types in a polymer, and by varying the molecular weight of the soft segment blocks. It is surmised that films and webs made from such fibers can be prepared that can also demonstrate other varying characteristics such as breathability and water transport, by varying the ratio of hard segment to soft segment in the polymer. For example, the soft segment responsible for the absorbency functionality in a polymer of the present invention is based on a component with polyalkoxy groups e.g. poly(oxyalkylene), such as a  
20 poly(oxyethylene) (PEG). PEGs may be obtained commercially under the brand name CARBOWAX® from the Union Carbide Corporation, South Charleston, West Virginia, from Crosby Chemicals, Metairie, Louisiana, or from Aldrich Chemical Co. Preferably the PEG compounds have a molecular weight of from about 600 to about 20,000, although they may  
25 run higher. If the molecular weight of the PEG is much below 600 the PEG will be a liquid at room temperature.

The soft segment responsible for the elasticity in the polymeric chain of the present invention is preferably based on a polyalkoxy component such as polytetramethylene ether glycol (PTMEG). PTMEG is commercially available in molecular weight ranges from 250-  
30 3000 from Dupont's Specialty Chemicals Division under the brand name Terathane. It should be appreciated that PTMEGs of larger molecular weight may be capable of being synthesized by a chain extension reaction utilizing an isocyanate in a reaction similar to a chain extension of a polyurethane chain. Preferably the PTMEG compounds have a molecular weight of about 2,000.

35 The linkages by which the soft segment reactants are covalently bonded to each other will be selected independently from the group consisting of urethane, amide, ester, and



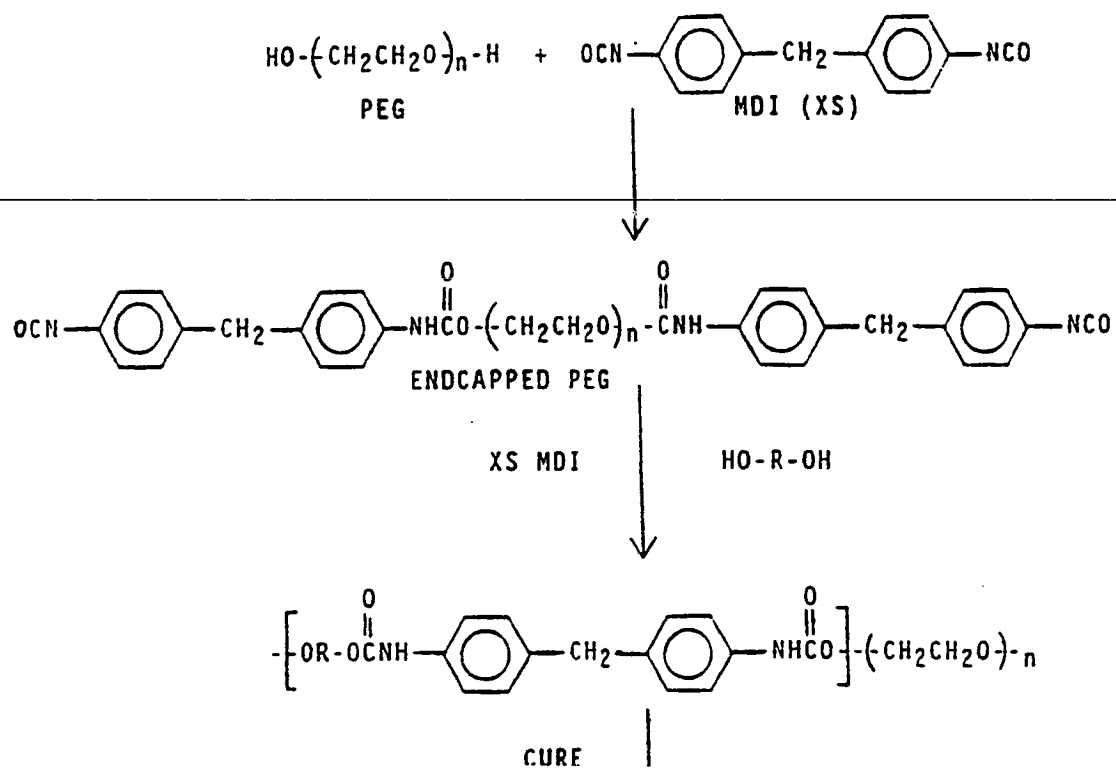
secondary urea linkages. The preferred functional groups of the first reactant of the soft segment are dihydroxy groups. The preferred functional groups of the second reactant are diisocyanate groups. Isocyanates such as Methylenediphenyldiisocyanate (MDI) are available from Aldrich ( MDI being represented by the following formula:

- 5  $\text{CH}_2(\text{C}_6\text{H}_4\text{NCO})_2$  ). It should be appreciated that if urea linkages are selected, the polymeric composition is less likely to be melt processable.

By way of illustration only, suitable diisocyanates which can be employed as the preferred second reactant include toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, ethylidene diisocyanate, propylene-1,2- diisocyanate, cyclohexylene-1,2-diisocyanate, 10 cyclohexylene-1,4-diisocyanate, m-phenylene diisocyanate, 4,4'-biphenylene diisocyanate, 3,3'-dichloro-4,4'-biphenylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6'-hexamethylene diisocyanate, 1,10-decamethylene diisocyanate, xylene diisocyanate, chlorophenylene diisocyanate, diphenylmethane-4,4'-diisocyanate, naphthalene-1,5-diisocyanate, cumene-2,4-diisocyanate, 4-methoxy-1,3-phenylene diisocyanate, 4-chloro- 15 1,3-phenylene diisocyanate, 4-bromo-1,3-phenylene diisocyanate, 4-ethoxy-1,3-phenylene diisocyanate, 2,4-diisocyanatodiphenyl ether, 5,6-dimethyl-1,3-phenylene diisocyanate, 2,4-dimethyl-1,3-phenylene diisocyanate, 4,4'-diisocyanatodiphenyl ether, benzidine diisocyanate, xylene-alpha, alpha'-diisothiocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate, 2,2',5,5'-tetramethyl-4,4'-biphenylene diisocyanate, 4,4'- 20 methylenebis(phenylisocyanate), 4,4'-sulfonylbis(phenylisocyanate), 4,4'-methylene di-o-tolylisocyanate, 1,4-bis(2-isocyanatoisopropyl)benzene, ethylene diisocyanate, trimethylene diisocyanate, mixtures thereof and the like.

Excess reaction compounds which may remain following a polymerization reaction are not a part of the soft segment. Therefore, any unreacted diisocyanate is considered to be 25 part of the hard segment.

By then using a chain extension reaction, the polymer chain can be lengthened. Such a chain extension reaction can be accomplished by reacting a diisocyanate such as MDI with a short chain diol, such as 1,4-butanediol in the presence of the soft segments. Butane diol (BDO) is available from J.T. Baker Chemical Co., Phillipsburg, New Jersey. These 30 reactions are illustrated by the following structural equation. It should be noted however, that as illustrated, the reaction is a single step polymerization. For greater control, the reaction can be done in two steps as described in the examples which follow. In a two step polymerization reaction excess MDI is not added, rather an amount is added to endcap or couple only. Then in a later step, more MDI is added to form the hard segment.



## POLYMER

By varying the ratio of MDI to PEG in the endcapping/coupling reaction, the soft segment length can be maintained or coupled together with other like or unlike soft segment chains. For example, a 2 : 3 mole ratio of PEG 8000 to MDI will yield an average soft  
5 segment molecular weight of approximately PEG 16,000. As a second example, PEG 2,000/PTMEG 2,000 (1 : 1 mole ratio) combined with MDI for a total diol/diisocyanate ratio of 4 : 5 will yield an average molecular weight of approximately 8,000 with a mixture of coupled PTMEG and PEG segments.

By varying the ratio of the various soft segment units within the polymer chain, the  
10 elasticity and/or absorbency can be increased. In particular, by varying the ratio of polyethylene glycol to polytetramethylene ether glycol (PTMEG) soft segments in a polymer chain, i.e a polyurethane chain, a polymeric material demonstrating both varying levels of absorbency and elasticity can be formed. By increasing the level of PTMEG soft segment percentage (while keeping the overall soft segment/hard segment ratio constant), materials  
15 of higher elasticity levels can be obtained.

The proposed method for synthesis of such polymers for incorporation into films, fibers, foams and injection-molded materials involves the use of a blend of chemicals to provide the soft segments that would be combined in the necessary ratio to then provide the desired amount of both absorbency and elasticity. As a further modification, other  
20 polyalkoxy compounds such as polyvinyl alcohol can be used to provide additional benefits.

A preferred thermoplastic polymeric composition having superabsorbent and elastic soft segments, and anchoring hard segments, can be prepared by the method which comprises the following steps:

- a) reacting a set of first compounds with a second compound (the amount of which is  
25 at least equal to the mole total for the set of first compounds) at a temperature of from about 50 to about 200 °C for a time sufficient to effect essentially a complete reaction; and
- b) reacting with the product of step (a) a third compound at a temperature of from about 50 to 200 °C for a time sufficient to obtain a polymer which is thermoplastic;  
30 in which said first compounds are difunctional poly(oxyethylene) and polytetramethylene ether glycol each having a molecular weight of from about 600 to about 20,000; said second compound is an aliphatic, cycloaliphatic, aromatic or heterocyclic compound having two functional groups which are reactive with the functional groups of said first compound; said third compound is an aliphatic,  
35 cycloaliphatic, aromatic, heterocyclic, or polymeric compound having two functional groups which are reactive with the functional groups of said second

compound; the reaction product of said first compound with said second compound, excluding excess second compound, forming the soft segments of the polymeric composition, and said third compound and said excess of said second compound forming the hard segments of the polymeric composition.

5 In the first step of the above method, the first set of compounds is reacted with the second compound at a temperature in the range of from about 50 to about 200 °C for a time sufficient to effect essentially complete reaction. The reaction temperature preferably will be in the range of from about 70 to about 120°C. and most preferably will be in the range of from about 70 to about 95 °C. While reaction time is not critical, typically the reaction time  
10 will be in the range of from about 20 minutes to about 3 hours when the reaction is carried out in the most preferred temperature range. In order to accomplish the reaction in the 20 minute time period, it would be necessary to use a catalyst.

The use of a catalyst will greatly determine the reaction time required. In general, isocyanates react easily with hydroxyl groups including polyols, however, the reaction rate  
15 will decrease with increasing size and number of substituents. Catalysts generally facilitate the kinds of polyurethane reactions described herein, but are not absolutely necessary. Typical reaction times for these 200-250 g reactions in the presence of one to three drops organotin compound catalyst may be 10-30 minutes. The catalyst can be added in the endcapping/coupling or the chain extension step. It is best to not go above  
20 80°C in the presence of catalyst since side reactions may occur, resulting in a loss of melt-processability. Without a catalyst, typical reaction times are 90-180 minutes (70-95°C). Other catalysts for the isocyanate and alcohol reactions are mild and strong bases such as sodium hydroxide, triamines, other organometallic compounds such as ferric acetylacetonate or cobalt naphthenate. The favored catalysts for forming the urethane  
25 linkage, however, are the organotin compounds described herein. For further discussion of such catalysts one should refer to Lambda, N. M. K., Woodhouse, K. A., and Cooper, S. L. Polyurethanes in Biomedical Applications, 1998, CRC Press, pp. 13-14.

Further, it is necessary to provide sufficient second compound to covalently link the first set of compounds with the third compound to give the polymeric composition of the  
30 present invention.

As already noted, the first set of compounds is most preferably a poly(oxyethylene) and polytetramethylene ether glycol. When such compounds are employed, the second compound is most preferably a diisocyanate and the third compound is most preferably a diol.

35 The second step of the method for preparing polymeric compositions involves reacting the product from the first step with a third compound at a temperature of from about 80 to

about 200°C. Preferably the reaction temperature will be from about 90 to about 150°C, and most preferably from about 70 to about 130 ° C for a time sufficient to obtain a polymer. Typically, this will result in a polymer with a melt flow rate of less than about 500g/10 minutes for processing temperature.

5           Although the use of a solvent usually is not necessary, one or more solvents may be employed in either or both steps if desired. For example, the use of a solvent may be convenient if the viscosity of the reaction mixture in the first step is too high to allow satisfactory mixing.

10           In general, any solvent can be used which is not reactive with any of the components of the reaction mixture and in which the reactants are sufficiently soluble. Examples of suitable solvents include, by way of illustration only, aliphatic ketones, such as acetone, methylethyl ketone, methyl propyl ketone, and the like; aliphatic esters of the lower aliphatic carboxylic acids, such as ethyl acetate, methyl propionate, butyl acetate, and the like; aliphatic ethers, such as diethyl ether, methyl propyl ether, and the like; aromatic  
15           hydrocarbons, such as benzene, toluene, the xylenes, and the like; halogenated aliphatic hydrocarbons, such as methylenechloride and the like; dioxane; tetrahydrofuran; dimethylformamide; N-methylpyrrolidone; and the like. The amount of solvent used is not known to be critical. However, a substantial amount of solvent preferably will not be present in the reaction mixture at the conclusion of the second step.

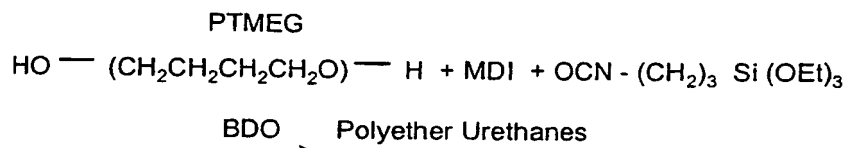
20           As already stated, it is preferred that the melt flow rate of the reaction mixture at the end of the second step should be less than about 500 g/ 10 minutes. The melt flow rate value is for a solvent-free reaction mixture. The target value of the melt flow rate is largely dependent upon the intended use for the resulting polymeric compositions. The melt flow rate values, are given by way of suggestion only.

25           A specific method for producing such a polymeric composition includes the steps of a) combining a sample of PEG with a sample of PTMEG in a suitable container, b) drying the samples, c) adding a diisocyanate to the container in an amount at least equivalent to the moles of the combined PEG and PTMEG samples, d) heating and stirring the sample, and e) adding additional diisocyanate and a short chain diol to the sample while stirring.

30           In another embodiment of the present invention, the resulting polymers can be made such that they are end-capped with a cross-linkable group, e.g. triethoxysilane. This allows the polymer to be melt-processable, so that it can be made into desired structures such as fibers or films, and then be post-treated to crosslink it to make it insoluble. One specific example would be to prepare a polyurethane polymer such that it was end-capped to have  
35           pendant groups such as triethoxysilane. The resulting polymer could then be made into nonwoven fibrous structures, and then be subsequently treated with a dilute acid solution by

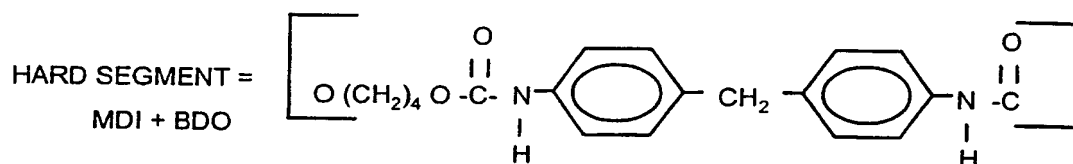
dipping the web in the solution. After this treatment, the web is insoluble but retains its original properties of elasticity. Such reaction is illustrated by the following structural equation in which MDI, PTMEG and triethoxysilane are reacted in the presence of BDO to form a polyether urethane. It should be noted that in a similar fashion the PEG soft segment

5 can also be endcapped by the triethoxysilane.



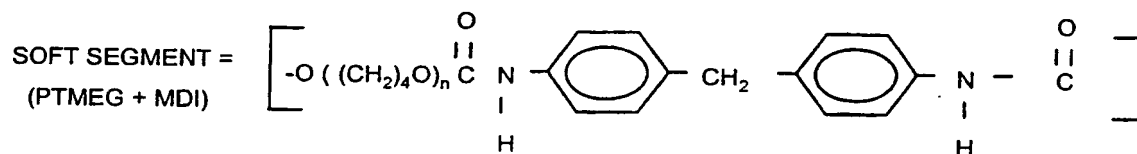
The hard segments in the reaction are represented by the following structural formula:

10



The soft segments in the reaction are represented by the following structural formula:

15



Essentially, in order to promote crosslinking in the polyurethane reaction a small amount of tri-functional material may be added at any step. For instance, the inclusion of triisocyanate at any step would induce crosslinking, as would the inclusion of a small amount of a triol at any step. Any one of these reactants would by itself induce crosslinking. It has been found that the mole amounts of the added materials do not have to be large and in fact it is preferred that they not be large with respect to the other materials. One example of the use of a trifunctional material to induce crosslinking would be to use such a material in combination with a greater amount of a difunctional compound. Alternatively, for thermal reversibility (which will be discussed in greater detail later in the application) both a diol and diisocyanate must be aromatic although only one of the two reactants need be trifunctional. It has been found that use of a slight excess of diisocyanate alone produces thermoplastic behavior in a product similar to that which results from a crosslinking reaction.

The present invention relating to PEG and PTMEG containing materials is further described by the following examples which illustrate preliminary reactions producing separate elastomeric and superabsorbent materials. Later examples illustrate prophetic synthesis reactions for forming single materials which are both elastic and superabsorbent followed by actual examples. Such examples are not to be construed as in any way as limiting either the spirit or scope of the present invention. In the examples, all temperatures are in degrees Celsius and all amounts are in parts by weight, unless otherwise specified. In each case where the resin kettle was heat dried, it was done so by passing a portable butane burner flame over the external kettle surfaces while purging the vessel with nitrogen.

It should also be noted that for the examples which follow, absorbcency/ superabsorbency values have been generated for absorption of water as opposed to saline solution, unless otherwise noted.

### Preliminary Examples

#### Synthesis of Separate Elastomeric and Superabsorbent Polymeric Materials

##### Example 1

##### Preparation of Polyether Urethane Thermoplastic Superabsorbent Polymer

##### Polymer Preparation:

A total of 212g (0.0148 moles) of polyethylene glycol (PEG), having a molecular weight ( MW ) of 20,000 g/mole, obtained from Union Carbide Corp., of South Charleston W.V. under the brand name CARBOWAX, was placed in a flame dried 500 ml resin kettle and melted and dried in a vacuum oven overnight at 60°C. Alternatively, this procedure may be accomplished in an oven for a minimum of 6 hours. The melted PEG (in the resin kettle) was then removed from the oven and equipped with a mechanical stirrer, a nitrogen inlet and a thermometer. 15.38 g (0.0615 moles) of methylene diphenyl diisocyanate (MDI) was then weighed under nitrogen and added to the kettle while stirring. The mixture was then stirred for approximately 2 hours at 90-110° C. To this was added 4.21 g (0.0467 moles) butanediol. The mixture was then stirred for approximately 2 hours at 90-130°C, until the observed viscosity increased significantly. The mixture was then poured into a Teflon ® coated pan. This polymer contained 7 % hard segment by weight and 93 % soft segment.

In some cases the PEG was first "endcapped" with MDI by putting 2:1 equivalents of MDI in the mixture first, and then adding the remainder with the chain extender, which in this case was butanediol. This reaction is typically followed by observing the disappearance of the isocyanate peak by infrared (at approximately 2250 cm<sup>-1</sup>). For additional molecular

weight, the polymers were placed in a vacuum oven at 80-85° C. The polymers were targeted to have melt flow rates of 100 g / 10 minutes at 195° C.

The resulting total polymer weight was 227 g., of which 15.89 g (0.0467 moles) was hard segment and 211.11 g (0.0148 moles) was soft segment PEG-MDI units.

5 The following equations were used to calculate the weight of each material:

$$0.0467 \times 90 \text{ g/mole} = 4.21 \text{ g BDO}$$

$$0.0148 \times 14,000 \text{ g/mole} = 207.2 \text{ g PEG}$$

$$0.0615 \times 250 \text{ g/mole} = 15.38 \text{ g MDI}$$

10

### Example 2

#### Preparation of Acid Crosslinkable Elastomeric Polyurethane

(20 % triethoxysilane groups, 15 % hard segments)

#### 15 Polymer Preparation:

A 500 ml resin kettle equipped with a mechanical stirrer, nitrogen, and air cooled condenser was flame dried. It was then charged with 190.15 grams (0.0951 moles, MW of 2000 g/mole) polytetramethylene ether glycol (PTMEG) which had been dried in a vacuum oven at 100° C, 1-2 mm Hg. A 10.19 g (0.0412 moles) sample of isocyanatopropyl triethoxysilane and a 41.20 g (0.1648 moles) sample of 4,4'-methylenebis (phenylisocyanate)(MDI) were then added in one portion. While constantly stirring the mixture, the kettle was heated using an oil bath at approximately 70° C. After 45 minutes, 9.98 g (0.1108 moles) 1,4-butane diol was added in one portion to the mixture.

20

25

After an additional hour, heating was stopped, although the mixture had not built up much observed viscosity. The mixture was left under nitrogen overnight. Heating was resumed the next day. The polymer was observed to have become very viscous and could no longer be stirred. The mixture was then removed from the resin kettle, spread into a glass crystallizing dish, and further heated at 100° C in a vacuum oven at 1-2 mm Hg. After six (6) hours, the polymer was removed.

30

#### Meltblowing Trial Using the Polymer:

The resulting polymer was placed in a miniextruder to produce meltblown polymer webs. The parameters of the miniextruder (approximately 100 g size) were set at the following conditions. The barrel temperature was set between 215-219° F. The coil



temperature was set at 225° F. Heat tape was used as needed. The air pressure was set at 10 psi and the air temperature was between 258-262° F at the nozzles.

The meltblowing trial produced good webs, although they were tacky. A portion of the web was then placed in a 10 % aqueous hydrochloric acid bath for 14.5 hours and then air dried. The web no longer melted up to 260° C. The web also seemed much stronger than before acid treatment, enabling it to be stretched without tearing.

### Example 3

#### Preparation of Acid Crosslinkable, Elastomeric Polyurethane (5 % triethoxysilane groups, 15 % hard segments)

##### Polymer Preparation:

A 500 ml resin kettle equipped with a mechanical stirrer, nitrogen, and air cooled condenser was flame dried. It was charged with 171.6 grams (0.0858 moles), MW of 2000 g/mole polytetramethylene ether ether glycol (PTMEG) which had been dried in a vacuum oven at 100° C, 1-3 mm Hg. The kettle was heated using a heating mantle to a temperature of approximately 70° C while stirring. A 2.30 g (0.0093 moles) sample of isocyanatopropyl triethoxysilane and a 44.15 gram (0.1766 moles) sample of 4,4' methylenebis(phenylisocyanate) (MDI) were then added in one portion. After 1.25 hours, the temperature was 72° C. Heating was increased slightly at this stage. Following another 1.25 hours, the temperature was 85° C. At this point, 9.01 grams (0.1001 moles) of 1,4 butane diol was added in one portion to the mixture.

Within 45 minutes the mixture had become very viscous. The viscosity had increased to the extent that the stirrer experienced difficulty mixing. The mixture was then removed from the resin kettle, spread onto a Teflon ® paper and stored in a sealed plastic bag. At a later time the polymer was pulverized using a mill to a mesh size of 5 mm. Prior to melt blowing, the pulverized polymer was dried under vacuum (approximately 2 mm Hg) at 50-60° C.

**Example 4****Preparation of Acid Crosslinkable, Elastomeric Polyurethane  
(10 % triethoxysilane groups, 15 % hard segments)****Polymer Preparation:**

Polymer was prepared by the method of Example 3 with the exception that the following amounts of reagents were used:

- 10            171.6 grams PTMEG (0.0858 moles)  
              9.01 grams 1,4 butanediol (0.1001 moles)  
              41.28 grams MDI (0.1673 moles)  
              4.60 grams isocyanatopropyl triethoxysilane (0.0186 moles)

**Example 5****Preparation of Acid Crosslinkable, Elastomeric Polyurethane  
(15 % triethoxysilane groups, 15% hard segments)****Polymer Preparation:**

20            Polymer was prepared by the method of example 3 except that the following amounts  
              of reagents were used:

- 171.6 grams PTMEG (0.0858 moles)  
              9.1 grams 1,4-butanediol (0.1001 moles)  
              39.50 grams MDI (0.1580 moles)  
25            6.90 grams isocyanatopropyl triethoxysilane (0.0279 moles)

**Example 6****Preparation of Acid Crosslinkable, Elastomeric Polyurea  
(20 % triethoxysilane groups) (exemplifying a solution-based  
30            reaction utilizing N-methylpyrrolidone solvent)****Polymer Preparation:**

              A 500 ml resin kettle equipped with a mechanical stirrer, nitrogen, addition funnel, and  
condenser was flame dried. It was charged with 50.0 grams (20 meq of calculated  
35            isocyanate groups) of an isocyanate-capped polytetramethylene ether ether glycol (capped  
PTMEG) and 300 ml N-methylpyrrolidone (NMP). This was heated with a heating mantle to

a temperature of 80° C. After approximately 20 minutes, 0.48 grams (or 16 meq) ethylene diamine in 10 ml NMP was added dropwise. After half of this solution was added, it was observed that a golden colored gel had formed. Heating was discontinued to allow the gel to re-dissolve in the NMP. Then 0.89 (4 meq) of 3-aminopropyltriethoxysilane was added dropwise. The resulting solution was stirred without heat for 1.5 hours.

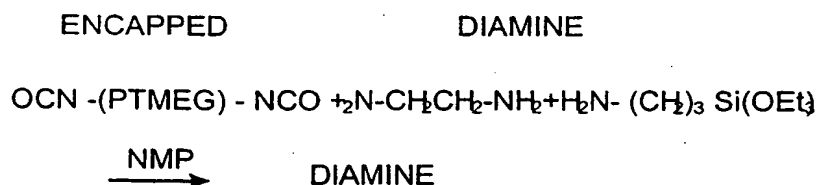
The solution was then removed, and films were cast onto glass plates using a doctor's blade. Another portion of the solution was acid-treated prior to casting films by mixing 10 grams of the solution with 1.5 grams ethanol and 3 drops 2N HCl solution. Films were cast after stirring this mixture for 10 minutes. Both sets of films (control and acid-treated) were dried under vacuum (100° C, 1-2 mm Hg ) to remove residual NMP prior to testing.

Example Instron results are as follows: (Instron processing crosshead speed set at 100 mm/minute; gage length =1 inch; grips = 1 inch x 3 inches rubber smooth; film thicknesses were recorded and varied from 0.003-0.006 inches).

TABLE 1

SAMPLE	%ELONGATION	STRESS (psi)	ULTIMATE MODULUS (psi)	%SET
V-No acid	720%	1800	240	10%
v-Acid	880%	3100	350	10%

The above reaction is generally illustrated by the following structural equation:



Examples: The following prophetic examples demonstrate processes for synthesizing superabsorbent and elastic polymers in accordance with the present invention

5

Synthesis of Single Polymeric Material

Having Both Elastomeric and Superabsorbent Attributes

Example 7

Preparation of 10 % Hard Segment Thermoplastic

10

Elastomeric/Superabsorbent Polymer

Similarly, an elastomeric and superabsorbent thermoplastic polymer is synthesized using the following procedure:

15

Polymer Preparation:

Calculation of Mole Ratio

mole ratio

50 wt % PEG at 8000g/mole soft segment	106 grams	0.0133 moles	1
50 wt % PTMEG at 2000g/mole soft segment	<u>106 grams</u>	<u>0.0530 moles</u>	4
	212 grams	0.0663 moles	

20

A 106 gram sample (0.0133 moles) of PEG at MW of 8000 g/mole is combined with a 106 gram sample (0.0530 moles) of PTMEG at MW of 2000g/mole in a flame dried 500 ml resin kettle and is allowed to dry overnight in a vacuum oven at 60° C. The melted soft segment is then removed from the oven and the kettle is then equipped with a mechanical stirrer, nitrogen inlet and thermometer. To the kettle is then added 16.58 grams (0.0663 moles) of MDI with stirring. The mixture is then stirred for approximately 2 hours at 110° C. Then 6.72 grams (0.0747 moles) of BDO and 18.68 grams of MDI is added. The mixture is then further stirred at 150° C for approximately two (2) additional hours and poured into a Teflon® coated pan.

25

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The 10 % hard segment amount is calculated according to the following equations:

$$\begin{aligned}
 1) \quad & \frac{(X \text{ amt. hard segment}) \times 100}{(212 \text{ grams} + 16.6 \text{ grams soft segment}) + (X \text{ amt. hard segment})} = 10 \\
 2) \quad & \frac{100 X}{(228.6 \text{ grams} + X)} = 10 \\
 3) \quad & 100X = 2286 + 10X \\
 4) \quad & 90X = 2286 \\
 5) \quad & X = 25.4 \text{ grams}
 \end{aligned}$$

### Example 8

#### Preparation of 5% Hard Segment Thermoplastic Elastomeric/Superabsorbent Polymer

A similar mixture is prepared using the same procedure as in Example 7, except that the amount of reagents is as follows:

<u>Calculation of Mole Ratio</u>			<u>mole ratio</u>
25 wt % PEG at MW 8000 g/mole (soft segment)	53 grams	0.0066 moles	1
75 % PTMEG at MW 2000g/mole (soft segment)	<u>159 grams</u>	<u>0.0795 moles</u>	12
	212 grams	0.0861 moles	

A 53 gram sample (0.0066 moles) of PEG 8000 g/mole is combined with a 159 gram sample (0.0795 moles) of PTMEG at MW of 2000g/mole in a flame dried 500 ml resin kettle and is allowed to dry overnight in a vacuum oven at 60° C. The melted soft segment is then removed from the oven and the kettle is then equipped with a mechanical stirrer, nitrogen inlet and thermometer. To the kettle is then added 21.53 grams (0.0861 moles) of MDI with stirring. The mixture is then stirred for approximately 2 hours at 110° C. Then 3.5 grams of BDO and 9.05 grams of MDI is added. The mixture is then further stirred at 150° C for approximately two (2) additional hours and poured into a Teflon ®coated pan.

The 5 % hard segment amount is calculated according to the following equations:

$$1) \quad \frac{(X \text{ amt. hard segment}) \times 100}{(233.53 \text{ grams soft segment}) + (X \text{ amt. hard segment})} = 5$$

$$2) \quad \frac{100X}{(233.53 \text{ grams} + X)} = 5$$

$$3) \quad 100X = 5(233.53) + 5X$$

$$4) \quad 95X = 1167.7$$

$$5) \quad X = 12.29 \text{ grams (0.0362 Moles)} = \text{approximately 3.25 g BDO and approximately 9.05 g MDI}$$

#### Example 9

#### Preparation of 5% Hard Segment Thermoplastic Elastomeric/Superabsorbent Polymer

A similar mixture is prepared using the same procedure as in Example 8, except that the amount of reagents is as follows:

#### Calculation of Mole Ratio

			<u>mole ratio</u>
50 % mole PEG MW at 8000	106 grams	0.0133 mole	1
50 % mole PTMEG MW at 2000	<u>26.6 grams</u>	<u>0.0133 mole</u>	1
	132.6 grams	0.0266 mole	

#### Polymer Preparation:

The mixture is prepared as described in Example 8 with 6.65 grams (0.0266 moles ) MDI. Later 1.845 grams (0.0205 mol) BDO and 5.125 grams (0.0205 mole) MDI are added. The mixture is stirred for two (2) more hours at between 90-130° C.

The 5 % hard segment amount is calculated in accordance with the previous equations:

$$6.98 \text{ g}/340 \text{ g/mole} = 0.0205 \text{ mol}$$

**Example 10****Preparation of 5% Hard Segment Thermoplastic  
Elastomeric/Superabsorbent Polymer**

5 A similar mixture is prepared using the same procedure as in Example 8, except that the amount of reagents is as follows:

**Calculation of Mole Ratio**

			<u>mole ratio</u>
	25% mole PEG MW at 8000	106 gram	0.0133 mole
10	75 % mole PTMEG MW at 2000	<u>79.8 gram</u>	<u>0.0399 mole</u>
		185.8 grams	0.0532 mole

**Polymer Preparation:**

15 The mixture is prepared as described in Example 8 with 13.30 grams (0.0532 moles) MDI. Later 2.59g (0.0288 mol) BDO and 7.59g (0.0288 mol) MDI are added. The mixture is stirred for two (2) more hours at between 90-130° C.

The 5 % hard segment amount is calculated in accordance with the previous equations:

$$9.78 \text{ g}/340\text{g/mole} = 0.0288 \text{ mol}$$

20

**Example 11****Preparation of 5% Hard Segment Thermoplastic  
Elastomeric/Superabsorbent Polymer**

25 A similar mixture is prepared using the same procedure as in Example 8, except that the amount of reagents is as follows:

**Calculation of Mole Ratio**

			<u>mole ratio</u>
	75 % mole PEG MW at 8000	106 grams	0.0133 mole
30	25 % mole PTMEG MW at 2000	<u>8.87grams</u>	<u>0.0044 mole</u>
		114.87grams	0.0177 mole

Polymer Preparation:

The mixture is prepared as described in Example 8 with 4.42g (0.0177 moles ) MDI. Later 1.59 grams (0.0177 mol) BDO and 4.42 grams (0.0177 mole) MDI are added. The mixture is stirred for two (2) more hours at between 90-130° C.

5 The 5 % hard segment amount is calculated in accordance with the previous equations:

$$6.05 \text{ g}/340\text{g/mole} = 0.0178 \text{ mol}$$

**TABLE 2**  
**SYNOPSIS OF PREVIOUS EXAMPLES**

<u>Example No.</u>	<u>Wgt% Hard Segment</u>	<u>Mole % Hard Segment</u>	<u>Proposed Property</u>	<u>Grams PEG</u>	<u>Moles PEG</u>	<u>Mol. Wgt. PEG</u>	<u>Grams PTMEG</u>
1	7	24%	Super Absorptivity	212	0.0148	14,000	0
2	N/A		Elasticity				
3	N/A		Elasticity				
4	N/A		Elasticity				
5	N/A		Elasticity				
6	N/A		Elasticity				
7	10	53	Super Absorptivity and Elasticity	106	0.0133	8,000	106
8	5	29.6	Super Absorptivity and Elasticity	53	0.0066	8,000	159
9	5	43.5	Super Absorptivity and Elasticity	106	0.0133	8,000	26.6
10	5	35.1	Super Absorptivity and Elasticity	106	0.0133	8,000	79.8
11	5	50	Super Absorptivity and Elasticity	106	0.0133	8,000	8.9

diphenyl diisocyanate = 250g/mole

butanediol = 90g/mole



<u>Example No.</u>	<u>Moles PTMEG</u>	<u>Mol. Wgt. PTMEG</u>	<u>WGT.% PEG/PTMEG</u>	<u>MOL.% PEG/PTMEG</u>	<u>Grams MDI</u>	<u>Moles MDI</u>	<u>Grams BDO</u>	<u>Moles BDO</u>
1	0	N/A	100.00%	100.00%	15.38	0.0615	4.21	0.0467
2								
3								
4								
5								
6								
7	0.053	2,000	50	20	35.26	0.141	6.72	0.0747
8	0.0795	2,000	25	8	30.58	0.1223	3.25	0.0362
9	0.0133	2,000	80	50	11.78	0.0471	1.84	0.0205
10	0.0399	2,000	57	25	20.5	0.082	2.59	0.0288
11	0.0044	2,000	92	75	8.84	0.0354	1.59	0.0177

### Example 12

#### Actual Example

Preparation of Triethoxysilyl endcapped PEG 3350

<u>5</u>	<u>Molar ratio</u>	<u>Weight ratio</u>	<u>Weight %</u>	<u>Actual weight</u>
1	X 3350	3350	87.1	131.5g
2	X249	498	12.9	19.5g

10 Gently heated dry tetrahydrofuran (THF) and PEG 3350 that had been dried in a vacuum oven over night under nitrogen until dissolved. Added tetramethyltriethoxysilylisocyanate dropwise over one hour and then refluxed approximately 10 hours or until isocyanate peak in infrared was no longer visible. A 20 ml portion of the solution was then placed in a beaker and 3 mls of 2 N HCl added. The material thickened within 5 minutes. A film was made of the material to give a stretchable and rubbery material before any evaporation. After drying under vacuum, a tough and strong nonelastic material was formed having an absorbency of 2.6g water/g. It should be understood that this type of reaction could be accomplished with either PEG, PTMEG or the combination such as in the polymer of the present invention.

20 For the following additional examples the 8000 PEG materials were obtained from Union Carbide Corporation and consisted of Century Grade NF, FCC ( food and cosmetic grade), Lot 2722. It has been found that certain lot numbers of higher molecular weight PEG soft segments obtained from certain distributors may contain unidentified extraneous impurities which interfere with the reactivity of the PEG soft segments. One method of addressing such impurities is to utilize benzoyl chloride as will be described herein.

25 Another approach would be to utilize "pure" high molecular weight PEGS available from

Polysciences, Inc, of Warrington, PA as starting materials, with or without the Benzoyl chloride. PEG 600, 1000, 1500, 2000 and 4500 are available from Aldrich. PEG 1000, 1450, 3350, 4000 and 4600 are also available from Union Carbide. PTMEG is available from DuPont as Terethane as Lot L20250426. PPG is also available from Aldrich, as is MDI, and Butane diol. The organotin compound catalyst Stannous 2-ethyl hexanoate and stannous octoate are available from ICN Biomedicals of Aurora, Ohio under Lot no. 6275A. Additionally, higher molecular weight PEG (up to 20,000 and more) are available from Shearwater Polymers, Inc. of Huntsville, Al., Shearwater being a distributor of polymers prepared by NOF Corporation of Japan.

**Example of Preferred Synthesis Procedure utilizing**  
**High Molecular Weight polyethylene glycol (PEGs)**  
**without polytetramethylene glycol (PTMEG)**

Soft segment polymers in each of the examples were first dried in a vacuum oven at between approximately 60-90 ° C (30mm Hg) for at least 8 hours prior to use. MDI was weighed in a dry box under argon gas.

The following synthesis procedure was used with PEG 8000 available from Union Carbide. A polymer resin kettle containing 261.15 g (0.0326 moles) vacuum dried (melted) PEG 8000 was equipped with a high torque mechanical stirrer and nitrogen inlet with bubbler, heating mantle, variac and thermocouple (between the resin flask and the mantle). To this was added 50 microliters of benzoyl chloride with stirring at 57.8 ° C. After approximately 1 hour, 16.32 g (0.0653 moles) of MDI was added with stirring at ca. 70 ° C. The mixture was stirred and maintained at approximately 69-77 ° C for ca. 2 hours to endcap the polymer. The polymer was then chain extended by adding 8.15 g (0.0326 moles) MDI with stirring followed (after mixing) by 5.876 g (0.0653 moles) BDO. Since the BDO is quite viscous, a small amount (less than 20 ml) of dry acetone was used to ensure quantitative transfer of the reagent. No catalyst was required in this reaction. After ca. 2 additional hours at approximately 71-77 ° C the reaction kettle was rapidly disassembled and the polymer melt poured onto a teflon foil coated casserole dish and placed in a vacuum oven at approximately 80 ° C for 20 hours. The absorbency was 8 g water/g polymer. This polymer became elastomeric at approximately 35 % water content. The polymer was completely thermoplastic and readily made a film and fibers.

It has been found that high molecular weight polymers often contain residual impurities such as potassium hydroxide, peroxides, aldehydes and aldehyde precursors besides the antioxidant BHA. Different grades and molecular weights will contain varying

amounts of these impurities, some of which can interfere with the polyurethane chemistry. A principal concern is the presence of residual potassium hydroxide. It has been found that the residual base can catalyze the homopolymerization of MDI and cause rapid irreversible solidification of the reaction mixture. To prevent this occurrence, adequate amounts of benzoyl chloride can be added to the MDI or to the PEG melt to neutralize any base present. It has been found helpful to thoroughly mix 50 microliters of the benzoyl chloride into approximately 200-250 g molten dried PEG prior to the addition of MDI. This procedure is necessary for PEG 4600 and higher. Occasionally, this practice is insufficient to prevent solidification. In such a situation, depending on the lot of PEG used, it may be necessary to use pure PEG starting materials. In the reaction it is also important to control the stoichiometry. In this regard, the molar ratio of isocyanate to diol should be close to a 1:1 ratio, with slight excess of diol. The diol component includes moles of both PEG and the chain extender diol. The ratio used in the preparations described was generally 1 : 1.02 isocyanate to diol. In this fashion, thermoplasticity is maintained, while assuring desired physical properties.

#### **Measuring the elasticity of PEG 8000 soft segment polymer.**

The minimum moisture for elasticity was determined by placing a piece of thin polymer film (pre-weighed) into a zip lock plastic bag in a plastic weigh dish. A moistened and wrung out paper towel was placed in the bag, but not in direct contact with the sample. Every few hours the polymer film was checked for elasticity by attempting to stretch the film. After approximately 24 hours the film became elastic and was weighed. The polymer film had absorbed 0.56 g water/g polymer (36% water). The film was then removed from the bag and water was allowed to evaporate. After approximately 30 minutes the film was no longer elastomeric. The film was again weighed and found to contain 0.11 g water/g polymer (9.6% water). It was therefore noted that the water swollen polymer was elastomeric while the polymer at ambient moisture levels was not.

While not intending to be limited thereby, it is theorized that water acts as a plasticizing agent to lessen the crystallinity and allow the polymer to become elastic and flexible. Other additives that could impart these same benefits without evaporation include for example, glycerin, low molecular weight PEGs and PPGs, and surfactants. Some of these materials would have the additional humectant property of retaining moisture in the polymer for added plasticization.

**Example of Preferred Synthesis Procedure utilizing  
polyethylene glycol (PEGs) with polytetramethylene glycol (PTMEG)**

PEG/PTMEG based materials were created using the reagents listed in Table 3.

The following general procedure was followed to produce the PEG/PTMEG materials. A

5 more specific synthesis procedure follows. A polymer resin kettle containing the allocated amount of vacuum dried (melted) PEG 8000 and PTMEG 2000 was equipped with a high torque mechanical stirrer and nitrogen inlet with bubbler, heating mantle, variac and thermocouple (between the resin flask and the mantle). To this was added between 35-

10 approximately 1 hour, the requisite amount of MDI was added with stirring at ca. 70°C.

The mixture was stirred and maintained at approximately 70-90 ° C for ca. 2 hours to endcap the polymer. The polymer was then chain extended by adding the requisite amount of MDI with stirring followed (after mixing) by the requisite amount of BDO. Since the BDO is quite viscous, a small amount (less than 20 ml) of dry acetone may optionally

15 be used to ensure quantitative transfer of the reagent. After ca. 2 additional hours at approximately 70-90 ° C the reaction kettle was rapidly disassembled and the polymer melt poured onto a Teflon® foil coated casserole dish and placed in a vacuum oven at approximately 80 ° C for 20 hours or other time frame as stated. A more specific

synthesis procedure includes the following steps: A polymer resin kettle containing 270g  
20 (0.034 moles) vacuum dried PEG 8000 and 90 g (0.045 moles) PTMEG 2000 was equipped with a high torque mechanical stirrer and nitrogen inlet with bubbler, heating mantle, variac and thermocouple (between the resin flask and the mantle). To this was added 35 microliters of benzoyl chloride with stirring at approximately 57.8° C. After approximately 1 hour, 23.62 g (0.095 moles) of MDI was added with stirring at ca. 70 ° C.

25 The mixture was stirred and maintained at approximately 69-77 ° C for ca. 2 hours to endcap the polymer. The polymer was then chain extended by adding 3.94g (0.0158 moles) MDI with stirring followed (after mixing) by 2.83 g (0.0315 moles) BDO. After ca. 2 additional hours at approximately 70-90 ° C the reaction kettle was rapidly disassembled and the polymer melt poured onto a Teflon® foil coated casserole dish and placed in a  
30 vacuum oven at approximately 80 ° C overnight: The absorbency of this polymer was 9g/g.

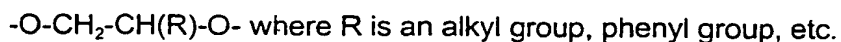
**Table 3**  
Samples of PEG and PTMEG Materials

Sample	PEG/ PTMEG	Moles PEG	Moles MDI	Moles BDO	Mole Ratios OH:NCO	Cure Cond. In Hrs. & °C
6676.24	PEG 8K PTMEG 2K	0.0687	0.1374	0.1100	1.3:1	—
6676.31	PEG 8K PTMEG 2K	0.0908	0.1090	0.0	1:1.2	20 hrs 80°C
6676.33	PEG 8K PTMEG 2K	0.0788	0.1103	0.0315	1:1	80°C 15 hrs

For the purposes of the above table the abbreviation "K" shall mean 1000, such that 2K shall mean 2000.

For sample number 6676.24, the material produced was very pasty and never gathered significant molecular weight. This is not surprising since the mole ratios were off somewhat. For sample number 6676.31, the material produced demonstrated an absorbency of 0.75 g/g. The material became crosslinked. Three drops of the catalyst were added to this material when it was around 94° C during the soft segment coupling reaction. This caused very rapid reaction and the observed crosslinking. A chain extension step to form the hard segment was not possible. In sample number 6676.33, the reaction was repeated without a catalyst to gain greater control. Out of the kettle, the sample disintegrated like paste after exposure to water. After curing conditions, the polymer, had much more integrity. When swollen, the polymer (after curing conditions) formed shreds of elastomeric material, almost as a rubbery hydrogel. When a film was made, the material appeared to become nonelastomeric. The polymer did not seem to be elastomeric when dry. The absorbency proved to be 9 grams per gram of polymer.

In an alternate embodiment, a low crystallinity polyether is synthesized by combining crystalline polyethers such as PEGs with PTMEG and with less crystalline polyethers such as, but not limited to polypropyleneglycol or other types of branched structures into the soft segment structure of the polymer. Such branched type of structure is reflected by the following structural formula:



In particular, higher molecular weight PEG soft segments may be preferably combined with PTMEG soft segments and PPG soft segments.

A preferred thermoplastic polymeric composition having superabsorbent and elastic soft segments, and anchoring hard segments, can be prepared by the method which comprises the following steps:

- a) reacting a set of first compounds with a second compound (the amount of which is at least equal to the mole total for the set of first compounds) at a temperature of from about 50 to about 200 °C for a time sufficient to effect essentially a complete reaction; and
- b) reacting with the product of step (a) a third compound at a temperature of from about 50 to 200 °C for a time sufficient to obtain a polymer which is thermoplastic; in which said first compounds are difunctional poly(oxyethylene), polytetramethylene ether glycol and polypropylene glycol each having a molecular weight of from about 600 to about 20,000; said second compound is an aliphatic, cycloaliphatic, aromatic or heterocyclic compound having two functional groups which are reactive with the functional groups of said first compound; said third compound is an aliphatic, cycloaliphatic, aromatic, heterocyclic, or polymeric compound having two functional groups which are reactive with the functional groups of said second compound; the reaction product of said first compound with said second compound, excluding excess second compound, forming the soft segments of the polymeric composition, and said third compound and said excess of said second compound forming the hard segments of the polymeric composition.

In the first step of the above method, the first set of compounds is reacted with the second compound at a temperature in the range of from about 50 to about 200 °C for a time sufficient to effect essentially complete reaction. The reaction temperature preferably will be in the range of from about 70 to about 120° C. and most preferably will be in the range of from about 70 to about 95 °C. While reaction time is not critical, typically the reaction time will be in the range of from about 20 minutes to about 3 hours when the reaction is carried out in the most preferred temperature range. In order to accomplish the reaction in the 20 minute time period, it would be necessary to use a catalyst.

As already noted, the first set of compounds is most preferably poly(oxyethylene) polytetramethylene ether glycol, and polypropylene glycol. When such compounds are employed, the second compound is most preferably a diisocyanate and the third compound is most preferably a diol.

The second step of the method for preparing polymeric compositions involves reacting the product from the first step with a third compound at a temperature of from about 80 to

about 200 °C for a time sufficient to obtain a polymer. Preferably the reaction temperature will be from about 90 to about 150 ° C, and most preferably from about 70 to about 130 ° C.

Although the use of a solvent usually is not necessary, one or more solvents may be employed in either or both steps if desired, as described above. For example, the use of a solvent may be convenient if the viscosity of the reaction mixture in the first step is too high to allow satisfactory mixing. The following examples demonstrate this combination.

**Synthesis of polytetramethylene glycol (PTMEG), polypropylene glycol (PPG), polyethylene glycol (PEG) soft segment polyurethane**

A superabsorbent and elastomeric PTMEG, PPG and PEG material identified as 6676.46 was prepared utilizing the following reagent mole calculations.

**Table 4**

Sample	PEG 8K PTMEG 2K PPG 1K	Moles SoftSeg	Moles MDI	Moles BDO	Mole Ratio OH:NC	Cure Cond Hrs & °C
6676.46	PEG 8K PTMEG 2K PPG 1K	0.0882	0.1324	0.0198	1:1.22	77°C 0,4,20 Hrs

The superabsorbent and elastomeric PTMEG, PPG and PEG material identified as 6676.46 was prepared utilizing the following actual procedures. Twenty microliters of benzoyl chloride was added with stirring to molten dried and mixed 51.27 (0.0256 moles) PTMEG, 50.77 (0.0508 moles) PPG and 94.00 g (0.0118 moles) PEG in a resin kettle equipped with mechanical stirrer, heating mantle, nitrogen inlet and outlet. The temperature was maintained at between approximately 65-70°C. After ca. 15 minutes 25.7 g (0.103 moles) of MDI was added with stirring to couple and endcap the polymer soft segment mixture. After ca. 30 minutes 2 drops of tin catalyst was added with stirring. After 15 more minutes at 70-75°C, 7.35 g (0.0294 moles) of MDI and 1.8302 g (0.0203 moles) of BDO was added to the reaction mixture to form the hard segment portion. It should be noted that slightly more BDO was added than is called for by the mole calculations listed above. After ca. 25 more minutes at 75-80°C the polymer was removed from the reaction kettle, a sample was removed, then the remainder was poured onto a Teflon® coated foil in a pyrex dish and placed in a conventional oven at 77°C for four hours at ambient pressure. A sample was again removed and then the remainder was evacuated and left in the oven for a further 16 hours at 77°C. Due to the ratio of

isocyanate to diol (1:1.22 OH:NCO) this reaction cross-linked and the product did not behave like a thermoplastic polymer. The absorbencies were 3.14, 2.35 g water/g polymer for the uncured (without curing conditions) and four hour cured (with curing conditions) polymer samples respectively. The absorbency of the twenty hour cured (with curing conditions) polymer was not measured.

The sample identified as 6676.46 which had been crosslinked for 4 hours was tested for elasticity. The sample, which was in the form of a film, was trimmed on the edges in order to produce relatively thin strips. The film was approximately 3/16 inch thick. Approximately 1/8 inch thick slices were cut from the film to produce the three test samples (each of which could be considered a foam) described in the following Table 5.

**Table 5**

SAMPLE #	WIDTH	LENGTH	WEIGHT	DENSITY
1	1/8 inch	5 inch	0.79 g	0.41g/cm <sup>3</sup>
2	1/8 inch	4 3/4 inch	0.78 g	0.43 g/cm <sup>3</sup>
3	1/8 inch	4 7/8 inch	0.66 g	0.35 g/cm <sup>3</sup>

The samples were then run through a series of elasticity tests using a Sintec tester. The load cell of the instrument at full scale was a 25 lb force and was made by Eaton Corp. of Troy, Michigan.

The Sintec tester was a SINTEC Model 1/S made by Sintec, a division of MTS Systems Corp, of Research Triangle Park, NC. The crosshead speed on the test was 3 inch/min; and the jaw separation was 1 inch. The cycle elongation was set to different values depending on the sample. Using the instrument, the sample was first extended a certain distance and then returned to zero extension in a cycle test. The crosshead stayed at the zero mark for approximately 2 seconds and then started moving again and the sample was extended to break. Data was taken at the respective elongations and also when the sample was taken to break.

Sample 1 was taken to 65 % elongation (cycled) and then returned to zero for approximately two seconds. The sample was then taken to break. The original jaw separation on the device was set at 1 inch. The samples were not marked to indicate the initial position in the jaws. It was noted that the sample demonstrated some slippage out of the jaws during the high elongation going to break. The results of the cycle test at 65 % are reflected in FIG. 1 which shows a graph illustrating a 65 % Cycle of Force in grams versus Percent Elongation demonstrating elasticity in the polymer of the first sample. FIG. 2 is a graph illustrating a 65 % Cycle and then extend to Break in Force in grams versus Percent Elongation in the inventive polymer of the first sample.



Sample 2 was taken to 117 % elongation (cycled) and returned to zero. The sample was marked at the 1 inch initial jaw separation. The sample was observed throughout the trial when it was elongating and the Sintec computer reported that it broke at approximately 12 inches. Actual physical measurements during the test showed approximately 8 inches between marks at the time of break, demonstrating the slippage. The distance between the marks was remeasured after approximately 10 minutes after the test was completed and it had been reduced to approximately 3 inches. From the data, the % Permanent Set after Break was calculated from the following equation:

$$\begin{aligned} \text{\% Permanent Set after Break} &= \frac{\text{final length(after 10 min)} - \text{initial length}}{\text{stretch length at break} - \text{initial length}} \times 100 \\ &= \frac{3 \text{ inch} - 1 \text{ inch}}{8 \text{ inch} - 1 \text{ inch}} \times 100 = 29 \% \end{aligned}$$

$$\text{\% Stretch} = 100 \times \frac{(8 \text{ inch} - 1 \text{ inch})}{(1 \text{ inch})} = 700 \%$$

FIG. 3 is a graph illustrating a 117 % Cycle of Force in grams versus Percent Elongation demonstrating elasticity in the inventive polymer of the second sample while FIG. 4 is a graph illustrating the 117 % Cycle and then to Break in Force in grams versus Percent Elongation in the inventive polymer of the second sample.

Sample 3 was cycled to 307 % and then to break. The sample was marked in the jaws of the instrument as in the earlier sample. Observation of the elongation indicated very little slippage on the 307 % extension. As the material was proceeding to break about 1/2 inch slippage was observed when at approximately 400 % elongation (5 inches).

Slippage continued from that point to break. The Sintec computer reported that the sample broke at approximately 1600 % or 17 inches. Physical observation and measurement indicated a stretch of approximately 8 inches between marks at the time of break for an actual elongation to break of 700 % . The marks were remeasured after approximately 30 seconds after break and the distance between the marks had returned to approximately 3 inches. The distance was again remeasured after 5 minutes from the time the sample broke and the distance between the marks remained at approximately 3 inches. FIG. 5 is a graph illustrating a 307 % Cycle of Force in grams versus Percent Elongation demonstrating elasticity in the inventive polymer, while FIG. 6 is a graph illustrating 307 % Cycle and then to Break in Force in grams versus Percent Elongation in the inventive polymer. The data demonstrating the elongation and breaking points for each of the samples is reflected in the following Table 6. For the purposes of the

following table, the Percent Permanent Set is defined as follows using the following formula.

The initial length of the sample is the initial jaw separation plus the distance the crosshead moves when at least 10 g is indicated on the load cell. The stretch length is the total sample length at maximum elongation during the cycle minus the initial sample length. The permanent deformation of the sample is the total length of the sample during the second extension when at least 10 g is indicated on the load cell minus the initial length of the sample.

$$\% \text{ Permanent Set} = 100 \times \frac{\text{Permanent Deformation}}{\text{Stretch Length}}$$

Table 6

SAMPLE #	1	2	3
WEIGHT	0.79g	0.78g	0.66g
Elongation 1 <sup>st</sup> Indicated 10g force	1%	1%	1%
Cycle elongation	65%	117%	307%
Load at cycle elongation, g	1900g	1770g	1900g
Return elongation when indicated 10 g force	18%	39%	114%
Up elongation when indicated 10 g force	11%	22%	76%
Peak elongation Computer (slippage)	1450%	1270%	1600%
Peak elongation observed	--	700%	700%
Peak Load (load measured at peak elongation)	3540 g	3070g	3700g
Permanent Set	16%	18%	24%

In a further alternate embodiment of the present invention absorbent and elastomeric thermoplastic polymers are synthesized in to contain covalent crosslinks to provide strength and other desired properties, yet are melt processable due to reverse degradation of these crosslinks during processing. Introduction of reversible polyurethane links into the polymer enables the use of low temperatures during processing. Such polymers may be melt-processed into meltblown, spunbond or film structures. During processing, the polymers are heated to temperatures high enough to cause reversible

controlled degradation of covalent bonds linking the polymer chains (actually cross-linking) into a three dimensional network. This temporary degradation of the crosslinks allows the normally high or non-melting polymer to be melt processable. However, after processing and upon cooling, the crosslinks reform to provide the desired strength and material properties. Such desired properties include strength, elasticity, absorbency, and/or insolubility. Additionally, the polymer backbone may also contain thermally-reversible bonds, allowing for even greater ease of processing regardless of the apparent molecular weight of the starting materials.

An example of such polymers are polyurethane structures which provide both absorbency and elasticity, such as those synthesized from PEG and/or PTMEG reacted with isocyanates. Polyurethane structures rely on a balance between hard segments and soft segments to provide desired properties. The hard segments, which consist of crystallizable units (typically formed from reaction of a short diol chain extender with a diisocyanate), often provide physical crosslinks to polyurethanes. Alternatively, the use of aromatic diols or tri-functional compounds, such as a tri-ol or tri-isocyanate to achieve covalent crosslinks may be used.

As a specific example, the crosslinks consist of linkages formed by the reaction of a phenolic hydroxyl group with an aromatic isocyanate group, so that the resulting bond is thermally reversible. As a second example, these same thermally reversible bonds are prepared from bi-functional compounds so that it is incorporated into the polymer chain backbone as well. In either case, the ratio of crosslinking agents can be varied to provide the desired amount of crosslinking. Cross-linking provides the insolubility and a certain amount of strength to the resulting material. Numerous examples of multifunctional isocyanates and diol chain extenders may be found in U.S. Patent Nos. 5,047,456, 5,219,974 and 5,491,210 each to Onwumere et al., previously referenced and incorporated by reference. As in the previous embodiments, excess reaction compounds which may remain following a polymerization reaction are not a part of the soft segment. Therefore, any unreacted isocyanate is considered to be part of the hard segment.

By then using a chain extension reaction the polymer chain can be lengthened. Such a chain extension reaction can be accomplished by reacting an aromatic isocyanate with an aromatic diol in the presence of the soft segments.

By varying the ratio of the various soft segment units within the polymer chain, the elasticity can be increased. In particular, by varying the ratio of polyethylene glycol to polytetramethylene ether glycol ( PTMEG) soft segments in a polymer chain, i.e a polyurethane chain, a polymeric material demonstrating both varying levels of absorbency and elasticity can be formed. By increasing the level of PTMEG soft segment percentage

(while keeping the overall soft segment/hard segment ratio constant), materials of higher elasticity levels can be obtained.

In this fashion the thermoplastic polymeric composition having superabsorbent and elastic soft segments, and anchoring hard segments can be prepared by the method

5 which comprises:

a) reacting a first set of compounds with a second compound at a temperature of from about 50 to about 200 °C for a time sufficient to effect essentially a complete reaction; and;

10 b) reacting with the product of step (a) a third compound at a temperature of from about 80 to 200 °C for a time sufficient to obtain a polymer which is melt processable;

in which said first set of compounds are difunctional poly(oxyethylene) and polytetramethylene ether glycol each having an average molecular weight of from about 600 to about 20,000; said second compound is an aromatic compound having two  
15 functional groups which are reactive with the functional groups of said first compound; said third compound is an aromatic compound having two functional groups which are reactive with the functional groups of said second compound; the reaction product of said first compound with said second compound, excluding excess second compound, forming the soft segment of the polymeric composition, and said third compound and said excess  
20 of said second compound forming the hard segments of the polymeric composition.

In the first step of the above method, the first compound is reacted with the second compound at a temperature in the range of from about 50 to about 200 °C for a time sufficient to effect essentially complete reaction. The reaction temperature preferably will be the range of from about 80 to about 150 °C. and most preferably will be in the range of  
25 from about 95 to about 120 °C. While reaction time is not critical, typically the reaction time will be in the range of from about 20 minutes to about 3 hours when the reaction is carried out in the most preferred temperature range. It is necessary to provide sufficient second compound to covalently link the first compound with the third compound to give the polymeric composition of the present invention.

30 As already noted, the first set of compounds are most preferably a poly(oxyethylene) and polytetramethylene ether glycol. When such compounds are employed, the second compound is most preferably an aromatic isocyanate and the third compound is most preferably an aromatic diol. Alternatively, a triisocyanate may be used as the second compound.

35 The second step of the method for preparing polymeric compositions involves reacting the product from the first step with a third compound at a temperature of from

about 80 to about 200 ° C for a time sufficient to obtain a polymer with a melt flow rate of less than about 500g/ 10 minutes at processing temperature. Preferably the reaction temperature will be from about 90 to about 150 °C, and most preferably from about 110 to about 130 ° C. Alternatively, low molecular weight PEGs of less than or equal to 600 can be used in the polymerization reactions.

Although the use of a solvent usually is not necessary, one or more solvents may be employed in either or both steps if desired as described in the earlier embodiments.

As already stated, the melt flow rate of the reaction mixture at the end of the second step should be less than about 500 g/ 10 minutes for processing temperature although the melt flow rate values are given by way of suggestion only.

Alternatively, low molecular weight PEGs having a molecular weight of less than or equal to 600, may be used in combination with PTMEG in the inventive polymers. Additionally, being that low molecular weight PEGs can serve as both absorbent and elastic soft segments, they may be used without PTMEG in inventive polymers which include aromatic isocyanate/ aromatic diol portions in the hard segments.

The present invention is further described by the following examples which illustrate preliminary reactions producing separate superabsorbent materials. A second example illustrates prophetic synthesis reactions for forming single materials which are both elastic and superabsorbent. Such examples are not to be construed as in any way limiting either the spirit or scope of the present invention. In the examples, all temperatures are in degrees C and all amounts are in parts by weight, unless otherwise specified. In each case where the resin kettle was heat dried, it was done so by passing a portable butane burner flame over the external kettle surfaces while purging the vessel with nitrogen.

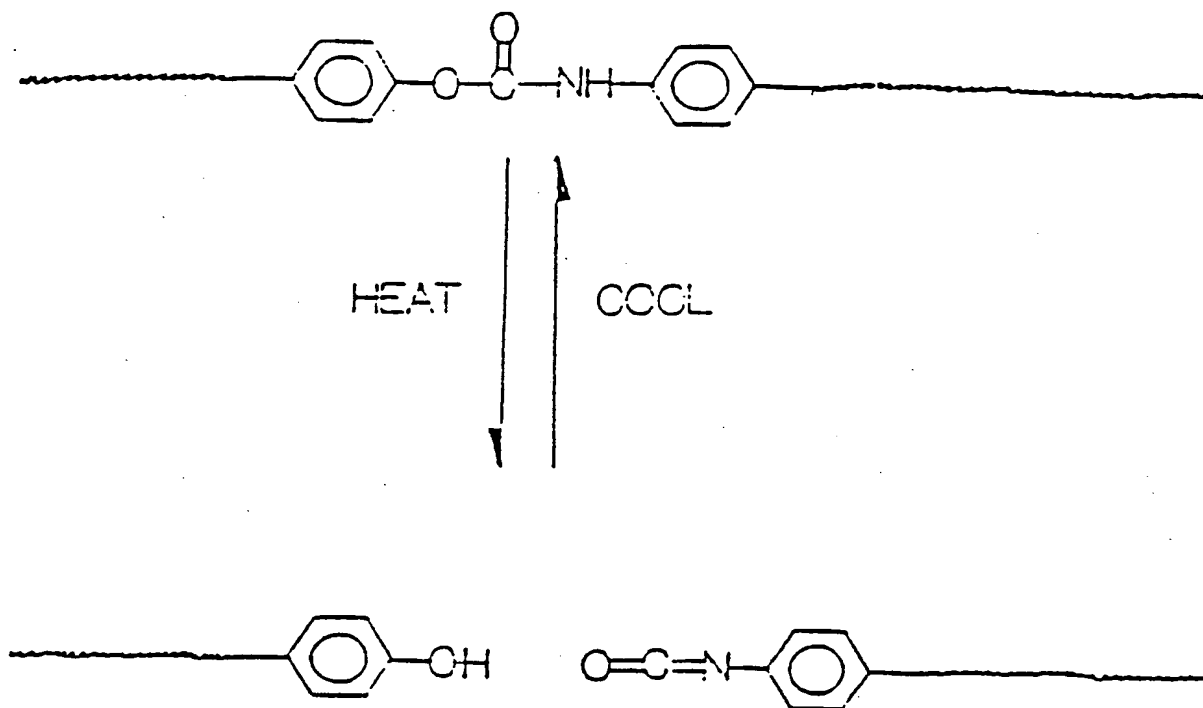
### Preliminary Examples:

#### Use of Thermally -Reversible Cross-linking for Preparation of Superabsorbent Materials

The polymer system used to prepare these thermally processable materials was a polyether urethane system. For the purposes of this example, the polyether moiety was termed the "soft segment" and was responsible for the hydrophilicity and absorbency of the polymer. The urethane moiety was termed the "hard segment" and was covalently bonded to the soft segment, insolubilizing the polymer in water so that it forms a gel rather than a water soluble material. The two components were immiscible and phase separate. The hard segment components crystallized together forming a "physical cross-link" that

was then melted and therefore processed. The hard segment components were prepared from methylene diphenyldiisocyanate and several types of diols.

The material was prepared via a three step process: Polyethylene glycol and Polyoxyalkylenediamine (Jeffamine ®) when present was first endcapped with an excess  
5 of methylenediphenyldiisocyanate (MDI). A diol chain extender was then added to form the hard segment. Finally the material was cured to complete the reaction. The reaction is generally as previously illustrated. If an aromatic diol is used as the chain extender, the polyurethane is thermally reversible. At 140-160 C° the urethane bond dissociates and two polymer chains are formed as illustrated in the following structural equation:



The reversible chemistry allows for the formation of polyurethanes that can be thermally processed at lower temperatures and higher throughputs. The urethane bond is reformed as the polymer is cooled below approximately 140° C. If PTMEG groups are added to the polymer chain, the polyurethane chain will then demonstrate both elasticity and absorbency.

#### Materials Utilized in the Preliminary Examples

##### Polymers utilized:

10 Polyethyleneglycol 8,000 (PEG 8,000), LC Grade, (CARBOWAX PEG-8,000, Union Carbide Corporation, South Charleston, West Virginia).

Polyethyleneglycol 8,000 (PEG 8,000), (Polyglycol E8000, The Dow Chemical Company, Midland, Michigan).

15 Polyethyleneglycol 14,000 (PEG 14,000) , (Union Carbide Corporation, South Charleston, West Virginia).

Polyethyleneglycol 20,000 (PEG 20,000) , (Crosby Chemicals,- Metairie, Louisiana).

Polyoxyalkylenediamine 2,000 (JEFF 2,000) , (JEFFAMINE® ED-2001, Texaco Chemical Company, Bellaire, Texas).

20 Polyoxyalkylenediamine 4,000 (JEFF 4,000), (JEFFAMINE ® 4,000, Texaco Chemical Company, Bellaire, Texas).

Methylenediphenyldiisocyanate (MDI), (Eastman Kodak Co., Rochester, New York).

4-Aminophenol (4-AP) , (Aldrich Chemical Co., Milwaukee, Wisconsin).

Hydroquinone bis (2-hydroxyethyl) ether (HBHE), Aldrich Chemical Co., Milwaukee, Wisconsin).

25 Methylhydroquinone (MHQ), (Aldrich Chemical Co., Milwaukee, Wisconsin).

Butanediol (BDO), (J.T. Baker Chemical Co., Phillipsburg, New Jersey).

#### Method of Polymer Preparation for Preliminary Examples

##### Reaction Conditions

30 A 500 mL, wide mouth resin kettle was charged with the polyethyleneglycol (PEG) and Jeffamine ® (when used) and dried overnight under vacuum at 100°C. The resin kettle cover with four ground glass flanges was dried in the oven or flame dried. The cover was attached and fitted with a nitrogen inlet, thermometer and high torque mechanical stirrer (Caframa, Type RZR50, CSA® Warton, Ontario, Canada; Fisher  
35 Catalog No. 14-500, Fisher Scientific, Pittsburgh, Pennsylvania). The kettle was flushed



with nitrogen and maintained under a nitrogen atmosphere. The reaction mixture was heated to 100°C and an excess of MDI was added. The reaction mixture was heated to and maintained at 120°C for 1 ¼ to 2 hours. The diol chain extender was then added and the reaction was allowed to stir rapidly for 15 to 30 minutes. The polymer was then  
5 poured into a Teflon® dish and placed under vacuum for 3 hours at 120°C. The material was allowed to cool slowly in the oven overnight under vacuum.

Film Superabsorbency Method

The polymers were melt-pressed at 140-145° C at 15,000 pounds per square inch to a thickness of 0.10 to 0.15 mm. The polymer was weighed and immersed in saline  
10 (0.9%) for the designated time (generally 3 hours) and removed onto a screen (15 mesh) on top of four layers of paper towel. The film was allowed to drain and then turned over to drain on the reverse side. The film was then weighed to the nearest milligram. The superabsorbency was calculated as follows and is shown in the column marked FILM:

15      
$$\text{superabsorbency} = \frac{\text{Weight of Polymer Plus Saline} - \text{Weight of Polymer}}{\text{Initial Dry Weight of Polymer}}$$

A listing of some alternative hard segment components includes  
methylenediphenyldiisocyanate, methylhydroquinone (MHQ), hydroquinine bis -2-  
20 (hydroxethyl) ether (HBHE), 4 aminophenol(4-AP), Butanediol. It was determined that the more effective the phase separation of the segments, the less hard segment necessary to insolubilize the polymer and the greater the absorbency that can be obtained. The following test data in Table 7 was produced from the samples:

**Table 7**  
Polymer Compositions (molar amounts)

<u>Ref.</u>	<u>PEG</u>	<u>JEFF</u>	<u>MDI</u>	<u>BDO</u>	<u>4-AP</u>	<u>MHQ</u>	<u>HBHE</u>
1	0.020 (8K)	0.008 (2K)	0.067	0.009		0.030	
2	0.020 (8K)	0.004 (2K)	0.044	0.005		0.015	
3	0.024 (8K)		0.070	0.011		0.036	
4	0.024 (8K)	0.005 (2K)	0.075	0.011		0.036	
5	0.025 (8K)	0.015 (2K)	0.089	0.009		0.038	
6	0.023 (8K)	0.019 (2K)	0.086	0.010		0.035	
7		0.101 (2K)	0.297	0.045		0.152	
8	0.160 (8K)	0.064 (2K)	0.336		0.064		0.048
9	0.020 (8K)	0.008 (2K)	0.042		0.008		0.006
10	0.020 (8K)	0.008 (2K)	0.034		0.006		0.000
11	0.020 (8K)	0.008 (4K)	0.042		0.008		0.006
12		0.040 (4K)	0.060			0.020	
13		0.040 (4K)	0.052			0.012	
14	0.020 (8K)	0.004 (4K)	0.047			0.023	
15	0.020 (8K)	0.004 (4K)	0.046			0.018	0.004
16	0.020 (8K)	0.004 (4K)	0.047		0.018		0.005
17	0.020 (8K)	0.004 (4K)	0.043				0.019
18	0.020 (8K)	0.004 (4K)	0.048		0.024		
19	0.020 (8K)	0.004 (4K)	0.041		0.013		0.003
20	0.020 (8K)		0.041		0.016		0.004
21	0.020 (8K)	0.008 (2K)	0.051		0.018		0.005
22	0.020 (8K)	0.004 (2K)	0.046		0.018		0.004
23	0.020 (8K)	0.002 (4K)	0.038		0.012		0.003
24	0.020 (8K)	0.002 (4K)	0.043		0.017		0.004
25	0.020 (8K)	0.008 (2K)	0.040		0.013		0.003
26	0.020 (8K)	0.004 (2K)	0.040		0.013		0.003
27	0.020 (8K)	0.008 (2K)	0.040		0.013		0.003
28	0.020 (8K)		0.035		0.012		0.003
29	0.020 (8K)	0.002 (4K)	0.038		0.012		0.003
30	0.020 (8K)	0.002 (4K)	0.044		0.017		0.004
31	0.020 (8K)		0.035		0.012		0.003
32	0.020 (8K)	0.004 (4K)	0.047		0.018		0.005
33	0.020 (8K)	0.004 (4K)	0.047		0.018		0.005
34	0.020 (8K)		0.035		0.012		0.003
35	0.020 (8K)	0.004 (4K)	0.041		0.017		
36	0.008 (20K)		0.023		0.015		

<u>Reference</u>	<u>Mole Ratios</u>	<u>Film</u>
14	ALL MHQ	22
15	4:1 MHQ: HBHE	15
16	4:1 4AP: HBHE	23
17	ALL HBHE	15
18	ALL 4-AP	19

1. All compositions contain 4.5% hard segment by weight, PEG 8k, MDI and 8.4% Jeff 4K.

From these example it can be seen that the key characteristic that determines the effectiveness of the hard segment and its influence on the properties of the polymer as a whole is its ability to phase separate from the soft segment. The more crystalline and rigid the hard segment the greater the gel strength of the polymer. The more effective the phase separation the less hard segment necessary to insolubilize the polymer and the greater the absorbency that can be obtained.

By varying the composition it was determined that polymers can be prepared solely with PEG soft segments that absorb up to 23 g saline/g polymer (Film Test). The percentage of soluble material after 3 hours of immersion in water was from 3 to 10%. Results of these experiments indicate that the hard and soft segment length and the rigidity of the hard segment components influenced the absorbency of these polymers.

The technique by which the polymers were prepared was kept constant throughout the experiments. However, it should be understood that variables such as order of addition of reagents, temperature, use of catalyst and cure time could be varied to change the characteristics of the end polymer. For instance, the use of a metal catalyst would cause the aromatic alcohols to react more rapidly than the aliphatic alcohols. Increasing the temperature will increase the possibility of side reactions such as allophanate and biuret linkages. The variables were generally not altered. However, in some of the experiments, a small amount of MDI was added initially to chain extend the soft segments before adding excess as in the written procedure. When this was done the polymer built up viscosity rapidly, presumably due to increased molecular weight.

In order to produce a superabsorbent and elastic thermoplastic polymer with high molecular weight PEG, PTMEG soft segments can be added to the polymeric chain in addition to the PEG soft segments. However, if low molecular weight PEG is used, PTMEG may not be necessary.

#### Method of Polymer Preparation for Prophetic Second Example

##### Reaction Conditions

A 500 mL, wide mouth resin kettle is charged with the polyethyleneglycol (PEG) and polytetramethylene ether glycol (PTMEG) and dried overnight under vacuum at 100°C. The resin kettle cover with four ground glass flanges is dried in the oven or flame dried. The cover is attached and fitted with a nitrogen inlet, thermometer and high torque mechanical stirrer (Caframa, Type RZR50, CSA® Warton, Ontario, Canada; Fisher Catalog No. 14-500, Fisher Scientific, Pittsburgh, Pennsylvania). The kettle is flushed with nitrogen and maintained under a nitrogen atmosphere. The reaction mixture is

heated to 100°C and an excess of an aromatic isocyanate is added. The reaction mixture is heated to and maintained at 120°C for 1 ¼ to 2 hours. The desired percent triol/aromatic diol chain extender, to give the desired amount of crosslinking, is then added and the reaction is allowed to stir rapidly for 15 to 30 minutes. The polymer is then  
5 poured into a Teflon® dish and placed under vacuum for 3 hours at 120°C. The material is allowed to cool slowly in the oven overnight under vacuum.

In additional alternate embodiments of the present invention the polyurethane reaction can be accomplished using reaction extrusion where the reagents are added and mixed in controlled amounts, reacted and then melt-processed to form, for example, films  
10 and fibers. The reaction is useful for this type of procedure since typically no water, alcohol or gaseous byproducts are formed. Small amounts of thermally reversible aromatic trifunctional cross-linking agent (e.g. triisocyanate or triol) can be added at a temperature above the dissociation temperature of the thermally reversible urethane bond. Upon cooling after processing into the desired form (e.g. fibers, films) the urethane  
15 bonds will form including some cross-links that will give the material greater strength and elasticity than was possible without covalent cross-linking. A post cross-linking step after the formation of the web can be accomplished using trialkoxysilyl groups in the parent polymer such as has been previously described. After melt-processing the material into the desired form, such as a nonwoven web, the material can be immersed in an acid bath  
20 and then air dried (and in a preferred embodiment heated to 100°C) to form siloxane cross-links.

A further alternate embodiment uses varying soft segment combinations with polymers containing polyurethane, polyester or other hard segments containing reactive groups that force the polymers to bend at varying angles, thereby preventing the longitudinal  
25 alignment and lessening large scale crystalline interactions.

An example of such a polymer is prepared with a mixture of PTMEG/PEG soft segments and polyurethane hard segments using toluene diisocyanate. Since this isocyanate is a mixture of the ortho and para substituted diisocyanate structures, the chains must link in a non-linear fashion, thereby minimizing long range interactions. This allows the  
30 resulting polymer to have greater elasticity from the PTMEG portion.

In a further alternate embodiment of the present invention, the elastic superabsorbent polymer (either thermoplastic or crosslinked) of the present invention, can also be used to form a coform material by extruding the polymer through a meltblown die tip and blowing additives into the meltblown air stream to be co-mingled with the meltblown fibers as  
35 described in U.S. Patent No. 4,100,324 to Anderson, et al. The possible additives include pulp, staple fibers, particulate, and the like. A pulp coform material with stretch and

recovery as well as superabsorbent properties would be highly preferred for absorbent products, e.g., diaper, adult incontinence, training pant, and the like.

Finally, it should be understood that other superabsorbents (SAMS) can be used in combination with the superabsorbent and elastic material of the present invention in order to produce a highly superabsorbent material.

The resulting polymer can then be processed to form fibers (e.g. meltblown or spunbond nonwovens), extruded into either monolithic or microporous films, produced into foam structures or injection molded into various structures. Additionally, the microporous films can be designed with pores that open and close with the desorption and absorption of water for a triggerable material.

In particular, nonwoven fabrics produced from fibers and films of the present invention may be used in composite elastic materials and multilayered laminates for use in personal care products such as diapers, where the absorbent material can function as a superabsorbent and elastomeric component. Other uses include therapeutic fabrics such as bandages and transdermal delivery systems, medical applications, agriculture, filtration, packaging, and wiping materials, and as novelty items.

The target value for the melt flow rate of the inventive polymeric compositions is largely dependent upon the use intended for the resulting composition. For example, if the composition is to be converted into a nonwoven web or fabric, the melt flow rate should be from about 20 to about 500g per 10 minutes, preferably from about 50 to about 400 g per 10 minutes, and most preferably from about 80 to about 300 g per 10 minutes. On the other hand, if the composition is to be extruded as a film, the melt flow rate of the final reaction mixture probably should be from about 10 to about 30 g per 10 minutes. The melt flow rate is determined in accordance with a slightly modified version of ASTM Test Method D1238-82, "Standard Test Method for Flow Rates of Thermoplastics by Extrusion Plastometer (Tinius Olsen Testing Machine Co., Willow Grove, Pa.). The modifications are as follows: (1) the sample is predried at ambient temperature under reduced pressure prior to loading; (2) the piston is not preheated; (3) the sample is loaded in 2-3 minutes; and (4) the loaded sample is preheated for 5 minutes. In every case, a 2.16 kg load is employed and the orifice diameter is  $2.0955 \pm 0.0051$  mm.

Such compositions are especially useful for the preparation of nonwoven webs by meltblowing and spunbonding processes, such as those described in U.S. Patent Nos. 3,016,599, 3,755,527, 3,704,198, 3,849,241, 3,341,394, 3,692,618, and 4,340,563 each of the foregoing patents being incorporated by reference herein in its entirety. Because the compositions of the present invention are particularly well-suited for the formation of nonwoven webs by meltblowing and spunbonding techniques, details of these processes

are provided hereinafter. However, the preparation of nonwoven webs by other methods is contemplated and comes within the scope of the present invention.

Referring now to the drawings where like reference numerals represent like structures or like process steps, and, in particular, to FIG. 7, which schematically illustrates one

5 embodiment of a process for forming a meltblown nonwoven web of a superabsorbent and elastomeric polymer made in accordance with the present invention, the superabsorbent, elastomeric thermoplastic composition is supplied in, for example, pellet form to a hopper 10 of an extruder 12. If desired, the polymer in the hopper 10 may be maintained under an inert atmosphere, such as nitrogen.

10 The temperature of the polymer is elevated within the extruder 12 by a conventional heating arrangement (not shown) to melt the polymer. Pressure is applied to the polymer by the action of a rotating screw (not shown), located within the extruder, to convert the polymer into an extrudable condition. The extrudable polymer then is forwarded by the pressure-applying action of the rotating screw to a melt blowing die 14. The elevated  
15 temperature of the extrudable polymer is maintained in the meltblowing die 14 by a conventional heating arrangement (not shown). The die 14 generally extends a distance which is about equal to the width 16 of the nonwoven web 18 which is formed by the process. The combination of the elevated temperature and elevated pressure conditions which affect extrusion of the composition will vary over wide ranges. For example, at higher  
20 elevated temperatures, lower elevated pressures will result in satisfactory extrusion rates and, at higher elevated pressures of extrusion, lower elevated temperatures will effect satisfactory extrusion rates.

The meltblowing die 14 includes an extrusion slot (not shown) which receives the extrudable polymer from the extruder 12. The extrudable polymer then passes through the  
25 extrusion slot (not shown) and through a plurality of small diameter capillaries 22 (as seen in FIG. 8) extending across the tip 24 of the die 14 in a linear arrangement, to emerge as molten threads 26 (shown in FIG 7). Preferably the polymer is extrudable at pressures of no more than about 300 psig in the die. Typically, such pressures will be in the range of from about 20 to about 250 psig. More typically, such pressures will be in the range of from  
30 about 50 to about 250 psig and most typically from about 125 to about 225 psig. Pressure in excess of these values may rupture or break some dies 14. Generally speaking, the extrudable polymer is extruded through the capillaries 22 of the die 14 at a rate from at least 0.02 grams per capillary per minute to about 1.7 or more grams per capillary per minute, typically from at least about 0.1 gram per capillary per minute to about 1.25 grams per  
35 capillary per minute. A more typical range is from at least about 0.3 grams per capillary per minute to about 1.1 grams per capillary per minute. The die also includes attenuating gas

inlets (not shown) which are provided with heated pressurized attenuating gas by attenuating gas sources 32 and 34. The heated pressurized attenuating gas enters the die 14 at inlets and follows a path through two chambers (not shown) and on through to narrow passageways or gaps so as to contact the extruded threads 26 as they exit the capillaries 22 of the die 14. The temperature and pressure of the heated stream of attenuating gas can vary widely. For example, the heated attenuating gas can be applied at a temperature of from about 100 to about 250° C. The heated attenuating gas can be applied at a pressure of from about 0.2 to about 20 psig, more specifically from about 0.5 to about 10 psig.

Generally speaking, it is preferred to utilize attenuating gas pressures of less than about 20 psig in conjunction with air passageway widths, which are usually the same. Lower attenuating gas velocities and wider air passageway gaps are generally preferred if substantially continuous fibers are to be produced. The two streams of attenuating gas converge to form a stream of gas which entrains and attenuates the molten threads 26, as they exit the linearly arranged capillaries 22, into fibers or, depending upon the degree of attenuation, microfibers (also designated 26) of a small diameter, to a diameter less than the diameter of the capillaries 22. The gas-borne fibers 26 are blown, by the action of the attenuating gas, onto a collecting arrangement which, in the embodiment illustrated in FIG. 7, is a foraminous endless belt 56 conventionally driven by rollers 57.

The distance of the collecting arrangement from the die tip (forming distance) must be sufficient to permit at least partial fiber solidification before the fibers contact the collecting arrangement. Because the forming distance is dependent upon the thermoplastic polymer per se, it is not possible to specify a precise range. However, the selection of forming distance is within the abilities of one having ordinary skill in the art, without the need for undue experimentation.

It should be noted, however, that the forming distance has only minimal importance, depending upon the circumstances. Such circumstances might include, by way of illustration, forming the nonwoven web on a carrier sheet which serves as a transporting means for the nonwoven web; the use of two or more meltblowing dies in series for the simultaneous production of a nonwoven web which can function as a carrier sheet; the use of one or more meltblowing dies in a series with one or more spunbond dies for the same purpose; and the like.

FIG. 7 illustrates the formation of substantially continuous fibers 26 on the surface of the belt 56. Other foraminous arrangements such as a drum arrangement may be utilized. The arrangement also may include one or more vacuum boxes (not shown) located below the surface of the foraminous belt 56 and between the rollers 57. The fibers 26 are collected as a fibrous nonwoven web 18 on the surface of the belt 56 which is rotating as

indicated by the arrow 58 in FIG. 7. The vacuum boxes assist in retention of the fibers 26 on the surface of the belt 56. Typically, the tip 24 of the meltblowing die 14 is from about 4 inches (about 10 cm) to about 30 inches (about 76 cm) from the surface of the foraminous endless belt 56 upon which the fibers 26 are collected. The thus-collected, entangled fibers 26 form a coherent, i.e. cohesive, fibrous nonwoven web 18 which may be removed from the foraminous endless belt 56 by a pair of pinch rollers 60 and 62 which may be designed to press the entangled fibers of the web 18 together to improve the integrity of the web 18. Thereafter, the web 18 may be transported by a conventional arrangement to a wind-up roll (not shown) for storage. Alternatively, the web 18 may be removed directly from the belt 56 by the wind-up roller. The web 18 may be pattern-embossed as by ultrasonic embossing equipment (not shown) or other embossing equipment, such as, for example, the pressure nip formed between a heated patterned calender and anvil roll (not shown) but as described in U.S. Patent No. 4,041,203 to Brock hereby incorporated by reference in its entirety.

FIG. 9 illustrates a generalized flow diagram showing one embodiment of a process for forming a spunbond nonwoven web made of a superabsorbent and elastomeric polymer in accordance with the present invention. As described in U.S. Patent No. 4,340,563 to Appel et al. which has been heretofore incorporated by reference in its entirety, the first step in a spunbonding process is to provide a thermoplastic polymer in fluid condition for spinning. Utilizing this process, it is important that the material be capable of being made sufficiently fluid for spinning and otherwise have the properties necessary to undergo drawing in a filament drawing zone.

The superabsorbent and elastomeric polymer is fed from a supply 60 to a hopper 62, then through extruder 64, filter 66, and metering pump 67 to spin box 68. Filaments are spun through spinnerette 72 with openings arranged in one or more rows forming a curtain of filaments 70 directed into a quench chamber 74. In the quench chamber 74 the filaments 70 are contacted with air or other cooling fluid through air inlet 76 and maintained cooler than said filaments, preferably near ambient temperatures, for example, in the range from about 40 to 130° F ( 4.4-54.4 °C). The quenching fluid is supplied under low pressure of less than 12 psi, preferably less than 2 psi, and a portion is preferably directed through the filament curtain 70 and removed as exhaust through port 78. As described above, the portion of air supplied that is discharged as exhaust will depend on the polymer being used and the rapidity of quenching needed to give desired filament characteristics such as denier, tenacity and the like. In general, the greater the amount of air exhausted, the larger the resulting fiber denier and, conversely, the lower the exhaust air ratio, the lower the denier.

As quenching is completed, the filament curtain is directed through a smoothly narrowing lower end 80 of the quenching chamber into nozzle 82 where the air attains a



velocity of about 150 to 800 feet per second. The drawing nozzle is full machine width and preferably formed by a stationary wall 84 and a movable wall 86 spanning the width of the machine. The movable wall can be retracted under the quench air screens or moved toward the stationary wall. During the start up, the wall is fully retracted so the filaments fall  
5 by gravity through the wide open nozzle. The low velocity of the incoming quench air is maintained through the wide open nozzle so little aerodynamic drawing actually occurs. When the polymer flow is fully established, the movable wall 84 is moved forward to decrease the nozzle 82 opening, increase the air velocity, and draw the filaments.

The position of the movable wall determines the drawing nozzle opening and thus the  
10 velocity of the air going through the nozzle for a given quench air flow rate and exhaust setting. The filament drawing force increases as the air velocity increases so the filament denier can be easily changed by simply increasing or decreasing the size of the nozzle opening. In general the filament denier can be increased by the steps of either enlarging the nozzle opening, reducing the air flow rate through the nozzle, increasing the exhaust air flow  
15 rate, lowering the quench air temperature, decreasing the polymer temperature, increasing the polymer molecular weight, e.g., decrease the melt flow rate, or increasing the polymer throughput per capillary. It should be noted that the first step reduces the air drawing force, while the third and fourth increase the polymer quench rate. The fifth and sixth steps increase the polymer extensional viscosity and the seventh step increases the mass of the  
20 polymer to be accelerated. The filament deniers can be changed relatively easily and rapidly in several different ways which do not affect the distribution of filaments out of the nozzle. In all cases, the nozzle spans the entire width of the machine. Therefore, a distribution of filaments corresponding substantially identically to the distribution of orifices in the spin plate across the machine width is maintained all the way to the outlet of the nozzle.

After exiting the nozzle, the filaments may be collected on a moving foraminous  
25 surface 88 such as an endless belt or screen to form a nonwoven web 90. By selecting the nozzle opening and forming distance, the dimensional characteristic of looping of individual filaments can be controlled to provide overlap of individual filaments. This results in a certain amount of intertwining and sufficient integrity in the resulting web. The web  
30 produced can then be compacted if desired through compaction rolls 91. The web 90 can then be thermally point bonded by rolls 92. The pair of bonding rolls 92 bonds the fibers together and increases the tear strength of the resultant web. One or both of the rolls are often heated to aid in bonding. Typically, one of the rolls is also patterned so as to impart a discrete bond pattern with a prescribed bond surface area to the web. The other roll is  
35 usually a smooth anvil roll but this roll also may be patterned if so desired. Following bonding the web can be stored on winder roll 94 for later use.

FIG. 10 is a perspective schematic view illustrating a second embodiment of a process for forming a spunbond nonwoven web made of a superabsorbent and elastomeric polymer in accordance with the present invention. The spunbond filaments can be produced in accordance with a spunbond process similar to that described in U.S. Patent No. 3, 802, 817 to Matsuki et al. hereby incorporated by reference. As shown in FIG. 10, filaments are extruded through a spinneret 100 having a large number of extrusion orifices 101 which are arranged into an elongated rectangular orientation, the length of which is selected to cover substantially the width of the nonwoven sheet 118. Beneath the spinneret 100 is positioned a draw unit 113 having a narrow elongated slit 114 passing completely through the draw unit.

From the extrusion orifices 101, the superabsorbent and elastic thermoplastic polymer is extruded in continuous monofilaments 115. The extruded filaments travel through an open air atmosphere. Under certain conditions the filaments may be cooled. The extruded filaments are introduced into the slit-like opening 114 in the form of a curtain.

By the application of an air supply 120 upon the filament curtain from both sides thereof, the extruded filaments are fed downwards from the spinneret into the draw unit at high speed, and are subjected to cold stretching. It should be recognized that air jets are not shown in the figure. The discharged filament curtain is then guided through the open air atmosphere along a distance and impinged upon a traveling collector shaped into an elongated endless belt or wire 116. In order to prevent disturbance in the formation of the filaments upon the collector it is preferable to keep the space below the collector at a negative pressure.

A process for forming a multilayered film utilizing a superabsorbent and elastic composition of the present invention is shown schematically in FIG. 11. Referring again to the figure, the multilayer film 222 of the inventive polymer is formed from a coextrusion film apparatus 200 such as a cast or blown unit. Typically the apparatus 200 will include two or more polymer extruders 201, at least one of which contains the inventive polymer. The multilayer film (usually a core layer and at least one skin layer) is extruded into a pair of nip or chill rollers 204 one of which may be patterned so as to impart an embossed pattern to the newly formed film 220. This is particularly advantageous to reduce the gloss of the film and give it a matte finish. Alternatively, the film can be extruded onto a single roll and is held in place by electrostatic pinners and/or vacuum boxes/ or blowers.

The film may then be further processed through stretching if it includes filler so as to create a microporous breathable film. Such is described in WO 96/19346 to McCormack and assigned to the same assignee as the present invention, hereby incorporated by reference. Alternatively the film may be wound onto winder 206.

The core and one or more of the skin layers may be filled and stretched so as to include micropores. In this embodiment, it is preferred that the skin layers be olefin-based. In this fashion, when water vapor passes through the skin layers, the absorbent and elastic core layer will swell thereby filling the stretched filled skin layer pores, and thereby creating a sealed barrier layer. It should be recognized that alternatively, a single film layer may be extruded of the polymer of the present invention.

FIG. 12 illustrates a cross-sectional view of a film laminate produced by the process illustrated in FIG. 11 with one side 260 representing the multilayered film including a core and two skin layers, and the other side 262 representing a nonwoven web support layer in a two layer film laminate.

In a further alternate embodiment, the previously described synthesis reactions are used to create absorbent, elastic foams. Such foams include both open and closed-cell foams. By using a foaming process, such as those used for preparing polyurethane foams, the resulting foams demonstrate both elastic and absorbent attributes. The foam structure itself provides additional benefit in the absorbent attributes of the foam material.

Foam production is accomplished by mixing the components under conditions such that the gaseous byproducts from polymerization (e.g. carbon dioxide) cause a porous, foam structure to form. The resulting foam structure has added benefits for additional applications beyond those already described, such as in materials where impact resistance or cushioning is desired. Furthermore, the addition of superabsorbent particles such as hydrogels, would provide additional absorbency enhancement.

The present invention therefore provides a single superabsorbent and elastic polymeric composition which is melt-processable. The polymeric composition provides for both uniform elasticity and absorbency in materials which can be melt-processed into fibers, films, foams and injection-molded articles. The absorbent and elastic composition provides superabsorbency without reliance on particulate hydrogels or separate absorbent and elastic components.

While the invention has been described in detail with particular reference to the preferred embodiments thereof, it should be understood that many modifications and additions may be made thereto, in addition to those expressly recited, without departure from the spirit and scope of the invention as set forth in the following claims.

**Claims**

What is claimed:

1. ~~A superabsorbent and elastomeric thermoplastic polymer comprising:~~
  - a) soft segment components each having a molecular weight in the range from about 600 to about 20,000 and selected from the group of PEG, PEO, PTMEG, PPG and PPO and combinations thereof and,
  - b) hard segments selected from the group consisting of polyurethanes, polyamides, polyesters, polyureas, and combinations thereof;wherein the soft and hard segments are covalently bound together by means of urethane, amide, ester or secondary urea linkages or combinations.
2. The superabsorbent and elastomeric thermoplastic polymer of claim 1 further including a plasticizer.
3. A nonwoven material comprising:
  - a) soft segment components each having a molecular weight in the range from about 600 to about 20,000 and selected from the group of PEG, PEO, PTMEG; PPG and PPO and combinations thereof and,
  - b) hard segments selected from the group consisting of polyurethanes, polyamides, polyesters, polyureas, and combinations thereof;wherein the soft and hard segments are covalently bound together by means of urethane, amide, ester or secondary urea linkages or combinations.
4. The nonwoven material of claim 3 further including a plasticizer.
5. The nonwoven material of claim 3 wherein said nonwoven material is a nonwoven web.
6. The nonwoven material of claim 5 wherein said material is a nonwoven meltblown web.
7. The nonwoven material of claim 6 wherein said meltblown web is a coformed web.

8. The nonwoven material of claim 5 wherein said nonwoven material is a spunbond web.
9. The nonwoven material of claim 3 wherein said nonwoven material is a film.
10. The nonwoven material of claim 3 wherein said nonwoven material is a foam.
11. A superabsorbent and elastomeric thermoplastic polymer comprising:
  - a) PEG and PTMEG soft segment components each having a molecular weight in the range from about 600 to about 20,000, and
  - b) hard segments selected from the group consisting of polyurethanes, polyamides, polyesters, polyureas, and combinations thereof;wherein the soft and hard segments are covalently bound together by means of urethane, amide, ester or secondary urea linkages or combinations thereof.
12. The superabsorbent and elastomeric thermoplastic polymer of claim 11 further including a plasticizer.
13. The superabsorbent and elastomeric thermoplastic polymer of claim 11 wherein said hard segments are selected from the group consisting of polyurethanes, polyamides, polyesters, and combinations thereof and wherein the soft and hard segments are covalently bound together by means of urethane, amide, or ester linkages or combinations thereof and said polymer is melt-processable.
14. A nonwoven material comprised of the superabsorbent and elastomeric thermoplastic polymer of claim 13.
15. A method of making a superabsorbent elastomeric thermoplastic polymer which comprises the steps of:
  - a) combining a sample of PEG with a sample of PTMEG,
  - b) drying the samples,
  - c) adding a diisocyanate to the PEG/PTMEG combination in an equivalent mole ratio for endcapping or coupling the PEG and PTMEG samples,

- d) heating and stirring the combination, and then
  - e) adding additional diisocyanate and a diol to the combination while stirring.
- 
16. A superabsorbent and elastomeric thermoplastic polymer comprising
- a) PEG , PTMEG and PPG soft segment components each having a molecular weight in the range from about 600 to about 20,000 ; and
  - b) hard segments selected from the group consisting of polyurethanes, polyamides, polyesters, polyureas, and combinations thereof wherein the soft and hard segments are covalently bound together by means of urethane, amide, ester or secondary urea linkages or combinations thereof.
17. The superabsorbent and elastomeric thermoplastic polymer of claim 16 further including a plasticizer.
18. The superabsorbent and elastomeric thermoplastic polymer of claim 16 wherein said hard segments are selected from the group consisting of polyurethanes, polyamides, polyesters, and combinations thereof and wherein the soft and hard segments are covalently bound together by means of urethane, amide, or ester linkages or combinations thereof and said polymer is melt-processable.
19. A nonwoven material comprising the superabsorbent and elastomeric thermoplastic polymer of claim 18.
20. A method of making a superabsorbent elastomeric thermoplastic polymer which comprises the steps of:
- a) combining a sample of PEG with a sample of PTMEG and PPG,
  - b) drying the samples,
  - c) adding a diisocyanate to the PEG/PTMEG/PPG combination in an equivalent mole ratio for endcapping or coupling the PEG, PTMEG, and PPG samples,
  - d) heating and stirring the combination, and
  - e) adding additional diisocyanate and a diol to the combination while stirring.
21. A superabsorbent and elastomeric thermoplastic polymer comprising:

- a) PEG and PTMEG soft segment components each having a molecular weight in the range from about 600 to about 20,000 ; and
  - b) hard segments selected from the group consisting of polyurethanes, polyamides, polyesters, polyureas, and combinations thereof; wherein the soft and hard segments are covalently bound together by means of urethane, amide, ester or secondary urea linkages or combinations thereof and wherein the hard segments include aromatic diisocyanate and aromatic diol portions.
22. The superabsorbent and elastomeric thermoplastic polymer of claim 21 further including a plasticizer.
23. The superabsorbent and elastomeric thermoplastic polymer of claim 21 wherein said hard segments are selected from the group consisting of polyurethanes, polyamides, polyesters, and combinations thereof wherein the soft and hard segments are covalently bound together by means of urethane, amide, or ester linkages or combinations thereof and said polymer is melt-processable.
24. A nonwoven material comprising the superabsorbent and elastomeric thermoplastic polymer of claim 23.
25. A method of making a superabsorbent elastomeric polymer which comprises the steps of:
- a) combining a sample of PEG with a sample of PTMEG,
  - b) drying the samples,
  - c) adding an aromatic diisocyanate to the samples in an equivalent mole ratio for coupling or endcapping the PEG and PTMEG,
  - d) heating and stirring the samples, and
  - e) adding additional aromatic diisocyanate and an aromatic diol to the sample while stirring.
26. A method of making a functionally crosslinked superasorbent elastomeric polymer which comprises:
- a) combining a sample of PEG with a sample of PTMEG in a suitable container,
  - b) drying the samples,

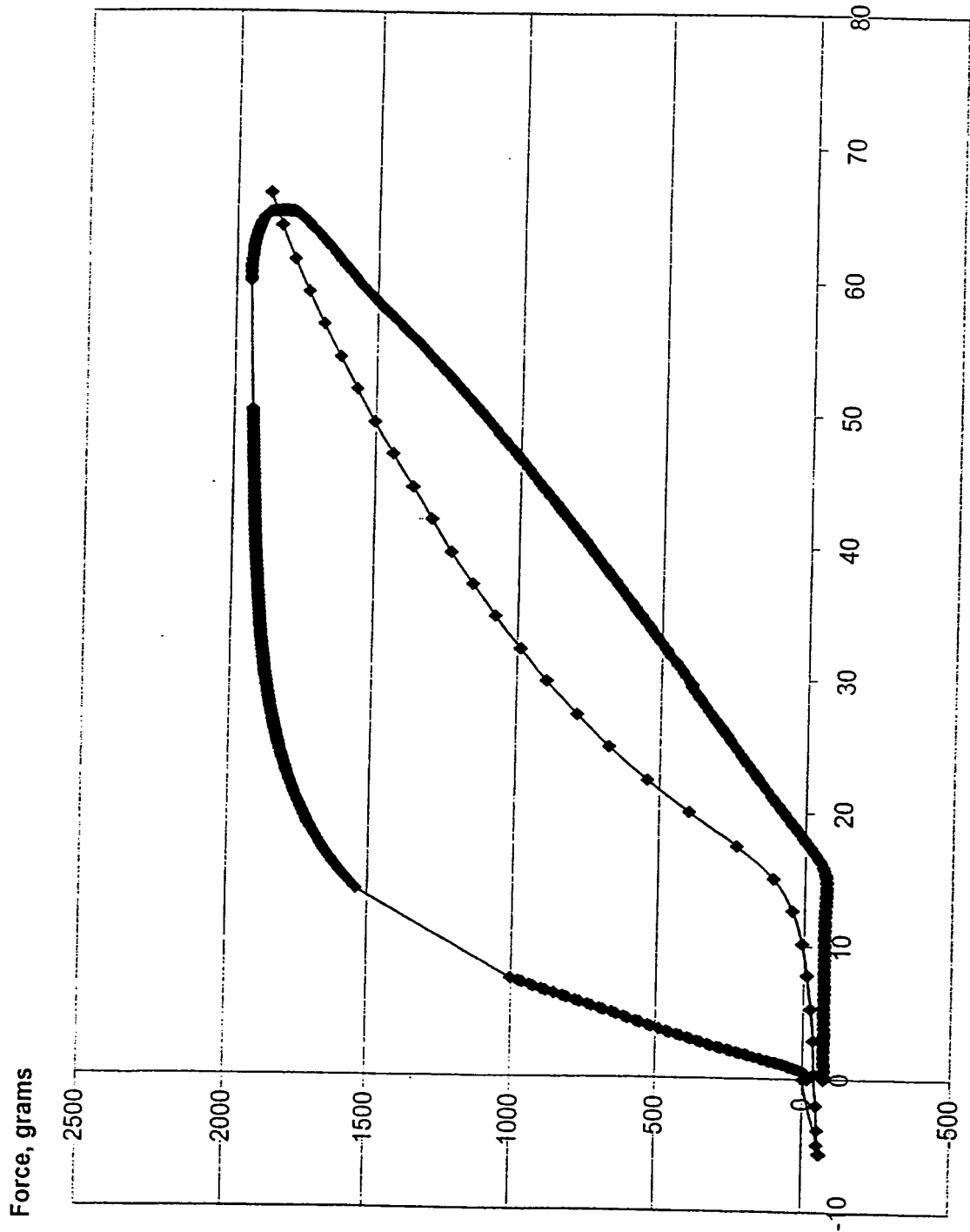
- c) adding a trifunctional reagent and/or diisocyanate to the container in an equivalent mole ratio for coupling or endcapping the PEG and PTMEG,
  - d) heating and stirring the sample,
  - e) adding additional trifunctional reagent and/or diisocyanate and an alcohol selected from the group consisting of diol and triol to the sample while stirring.
- 
27. The method of claim 26 wherein said trifunctional reagent is triisocyanate.
28. A method of making a functionally crosslinked superabsorbent elastomeric polymer which is crosslinked in postprocessing, comprises:
- a) combining a sample of PEG with a sample of PTMEG in a suitable container,
  - b) drying the samples,
  - c) adding a monofunctional reagent with a post treatment crosslinking group and a diisocyanate in the container,
  - d) heating and stirring the mixture,
  - e) adding an alcohol selected from the group consisting of diol and triol to the sample while stirring,
  - f) processing the resulting polymer into a desired polymer material, and
  - g) post treating the polymer material by exposing it to aqueous acid, either with or without heat.
29. The method of claim 28 wherein the monofunctional group contains a triethoxysilane as the post-treatment crosslinking group.
30. The method of claim 29 wherein said triethoxysilane is present in the range of between 5-40 % of the mole total of diisocyanate.
31. The method of claim 30 wherein said triethoxysilane is present in the range of between 5-20 % of the mole total of diisocyanate.
32. A method of making a superabsorbent elastomeric thermoplastic polymer which comprises the steps of:



- a) combining a sample of PEG with a sample of PTMEG,
- b) drying the samples,
- c) adding a diisocyanate to the PEG/PTMEG combination in an equivalent mole ratio for endcapping or coupling the PEG and PTMEG samples,
- d) heating and stirring the combination, and then
- e) adding additional diisocyanate and a diol to the combination while stirring, and
- f) adding a plasticizer to the completed polymer while stirring.

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Series1



Percent Elongation

FIG. 1

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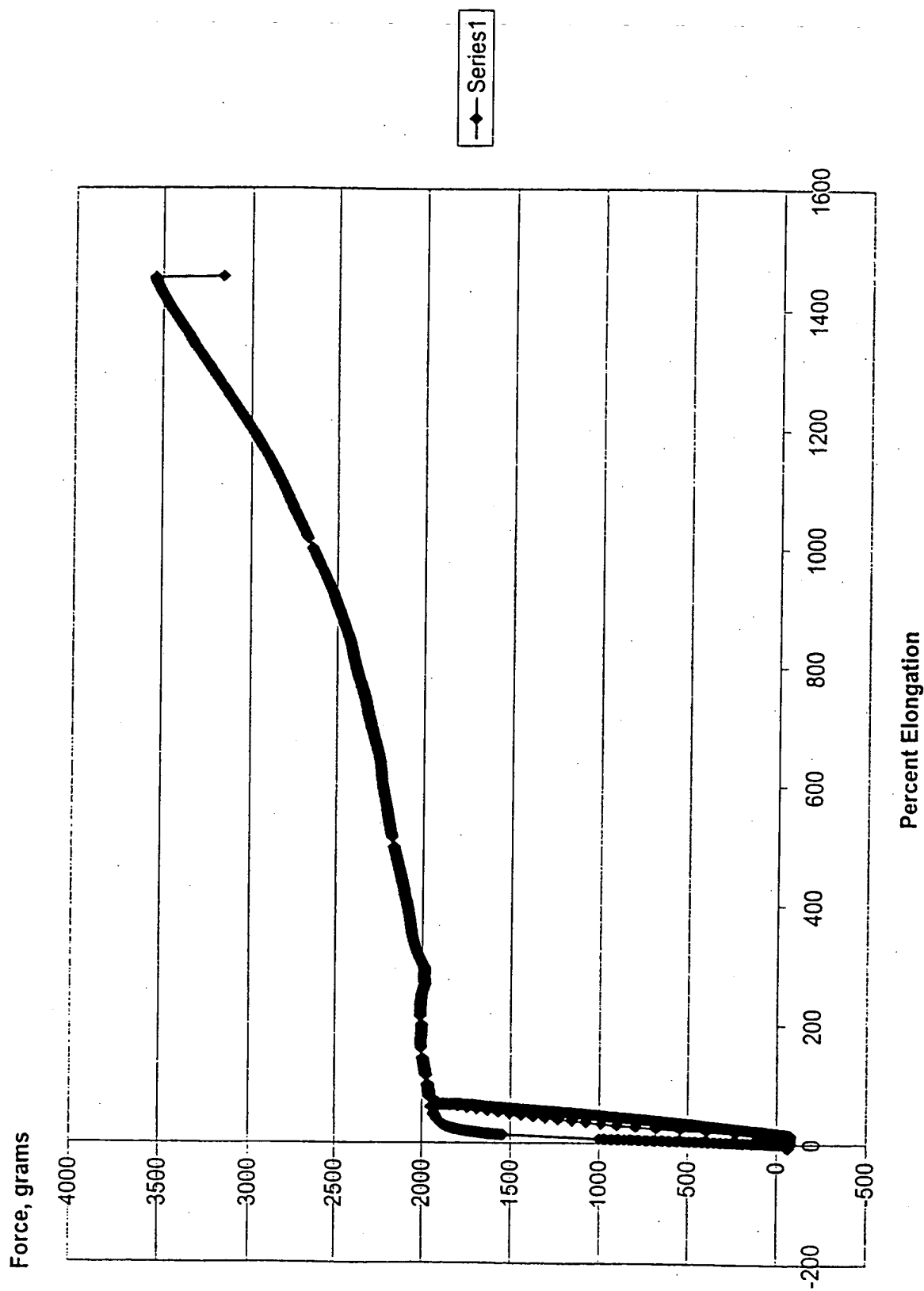
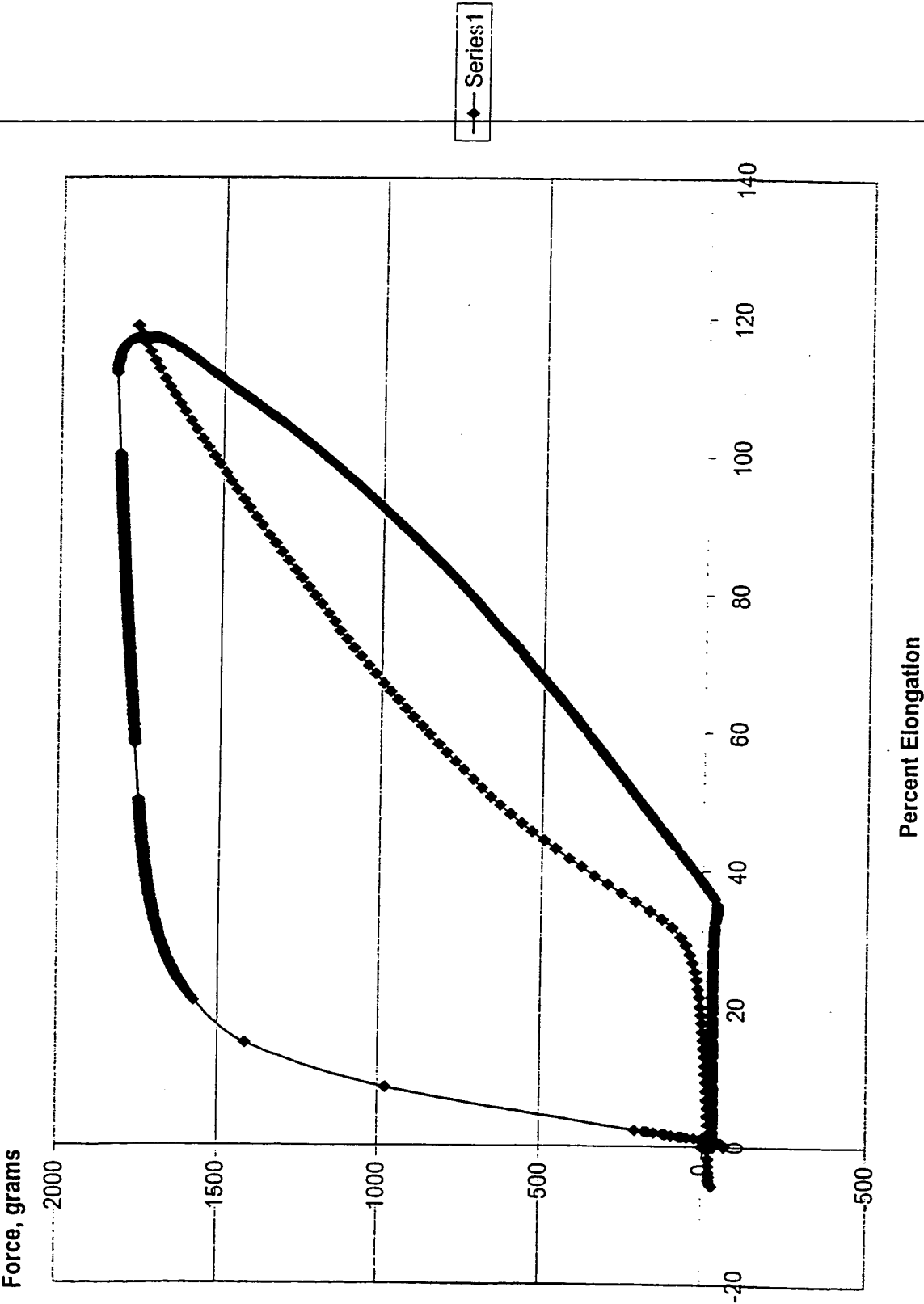


FIG. 2

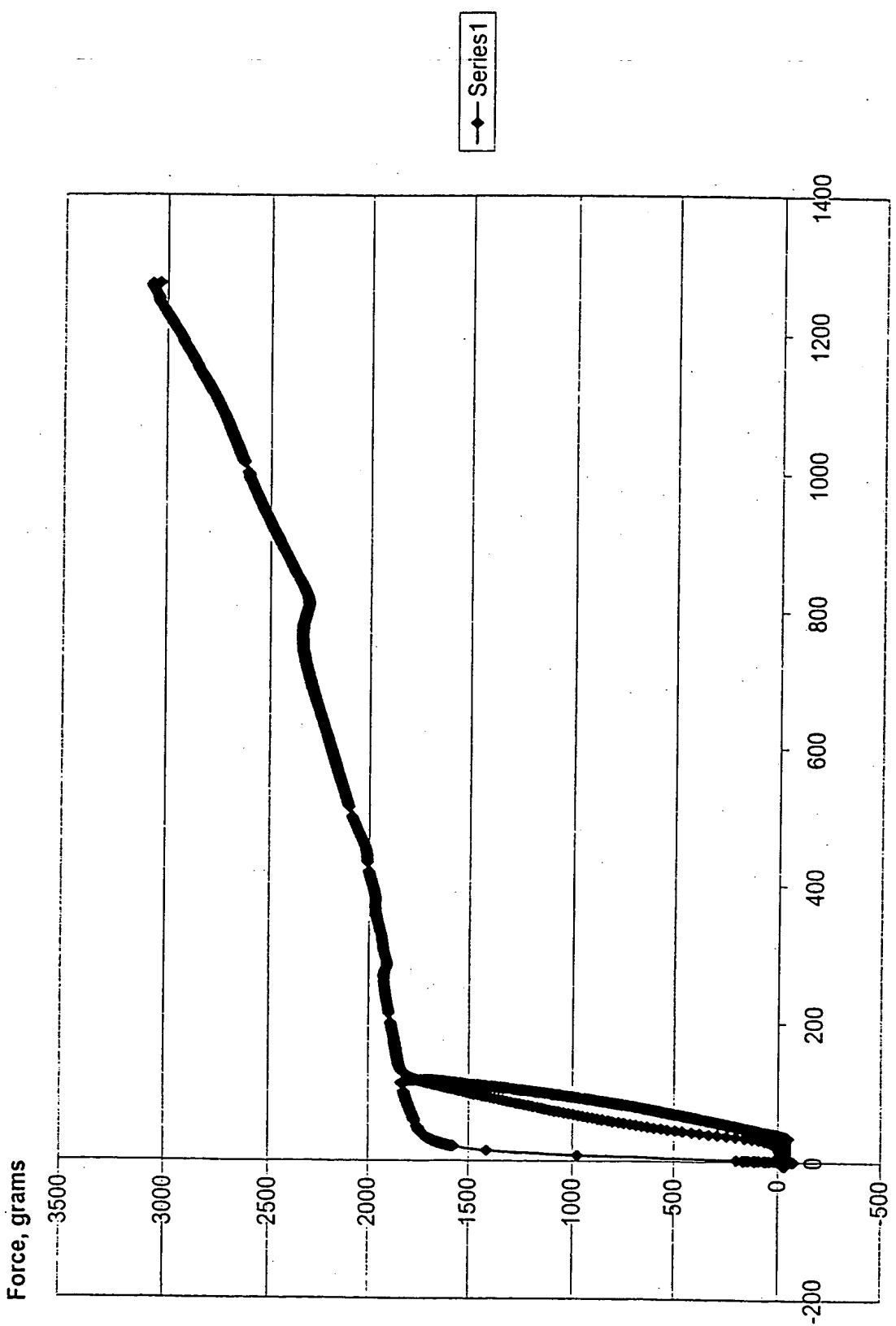
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Percent Elongation

FIG. 3

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Percent Elongation

FIG. 4

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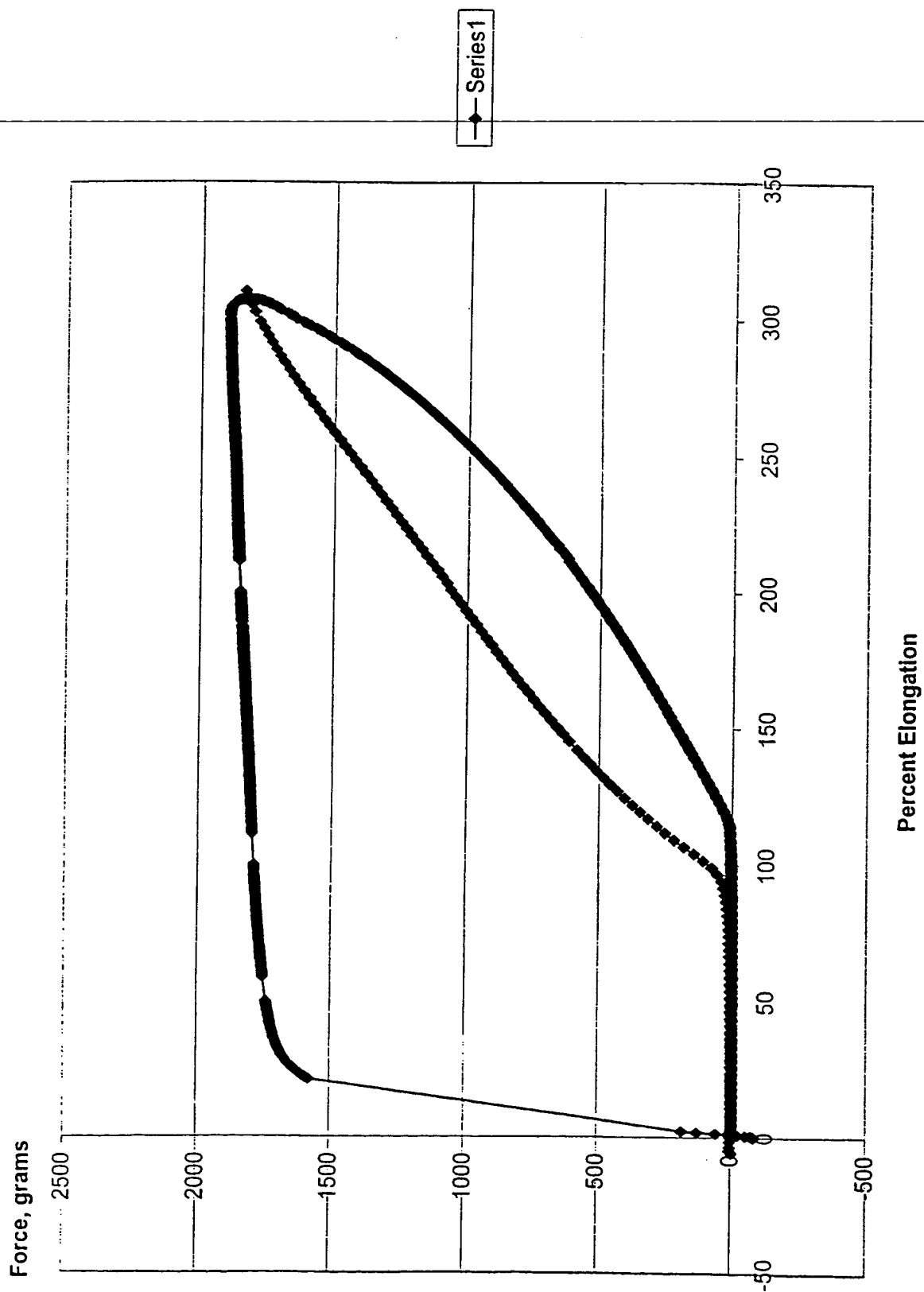
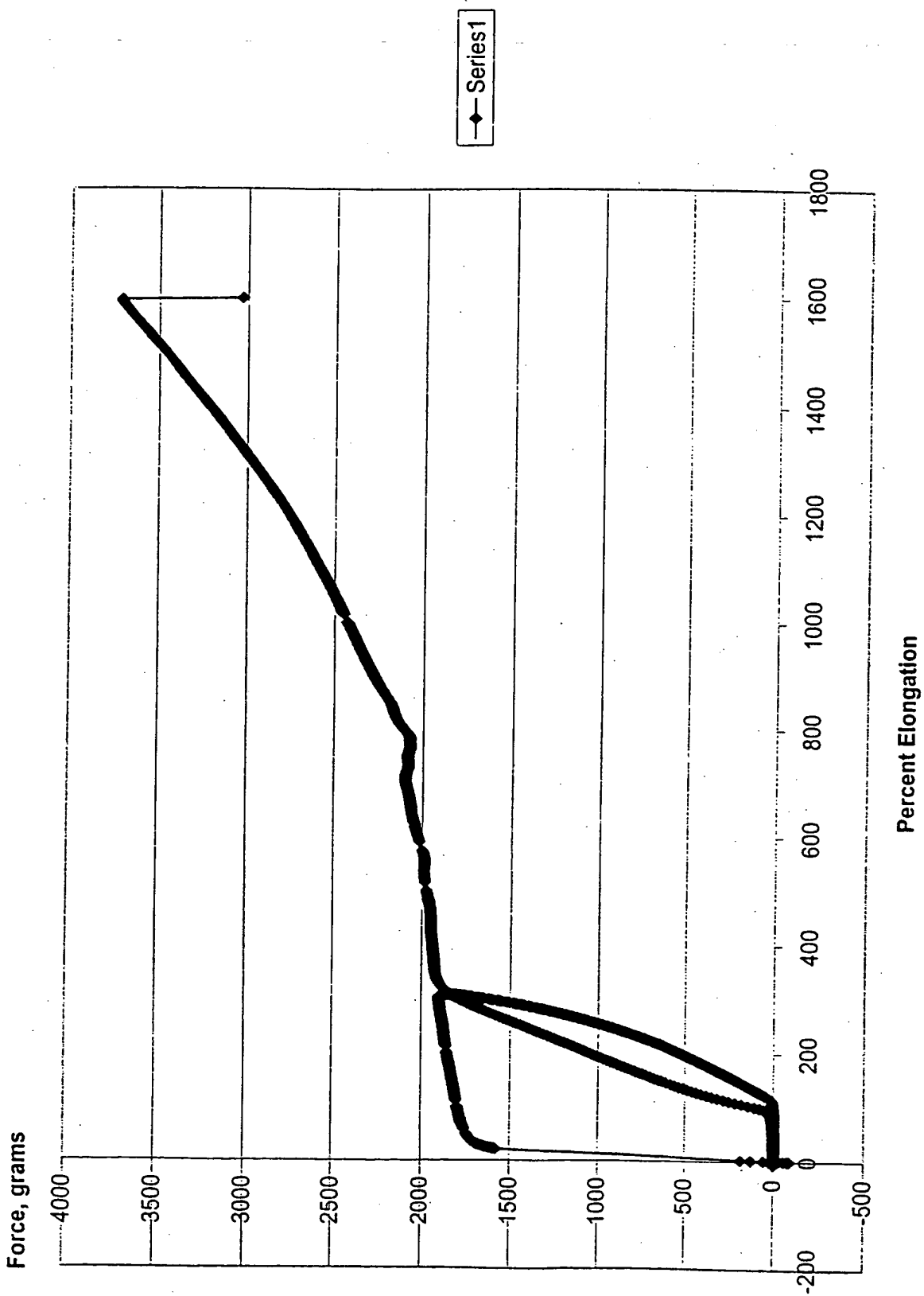


FIG. 5

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Percent Elongation

FIG. 6

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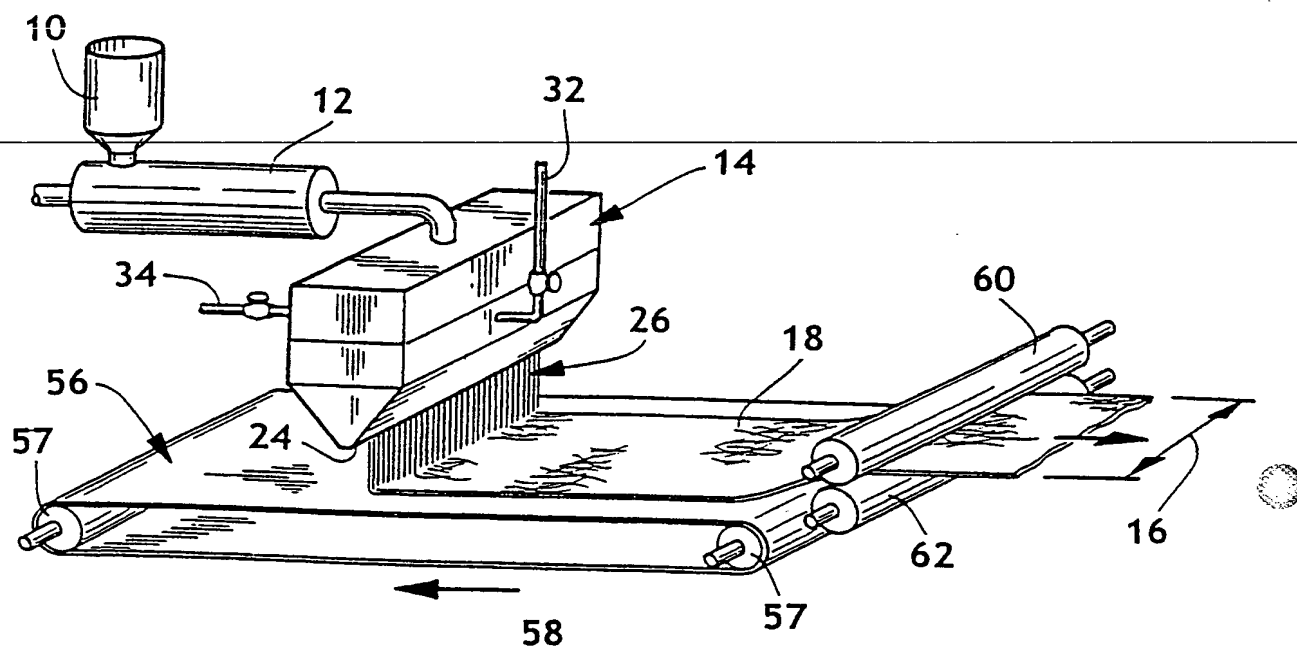


FIG. 7

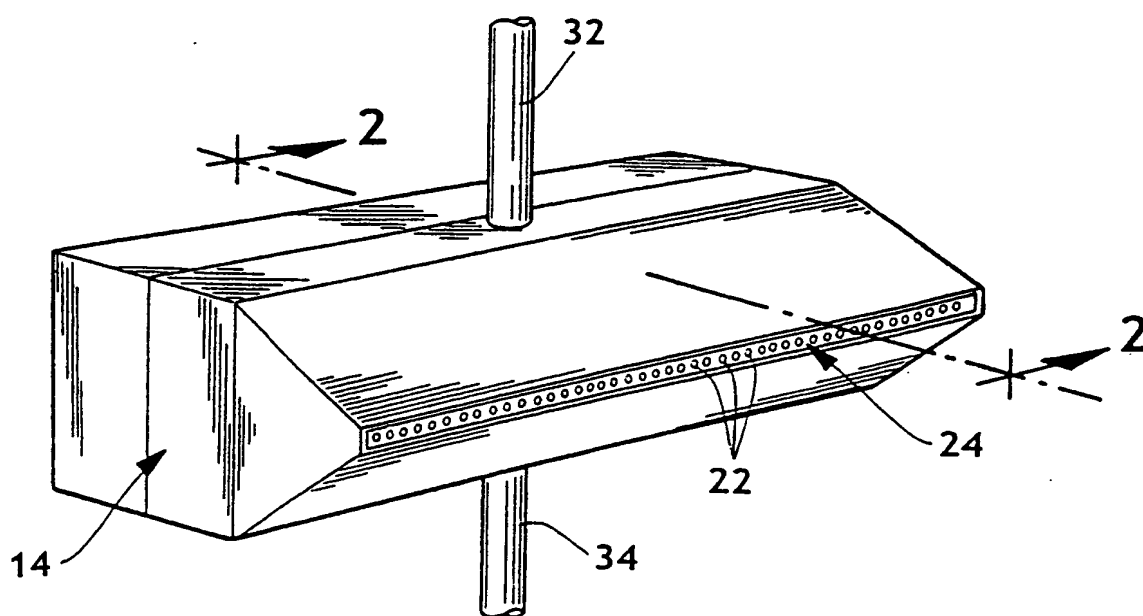


FIG. 8



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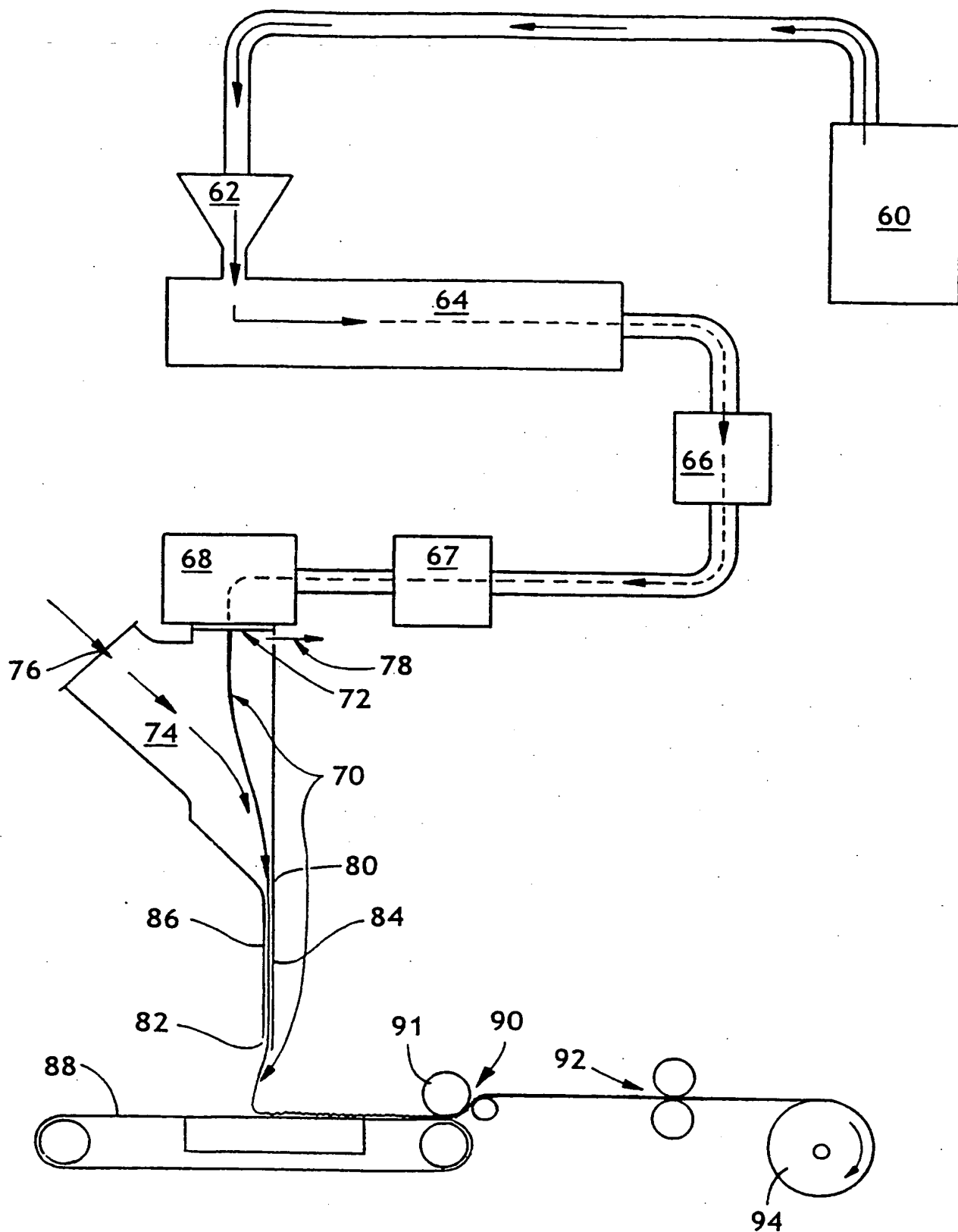


FIG. 9

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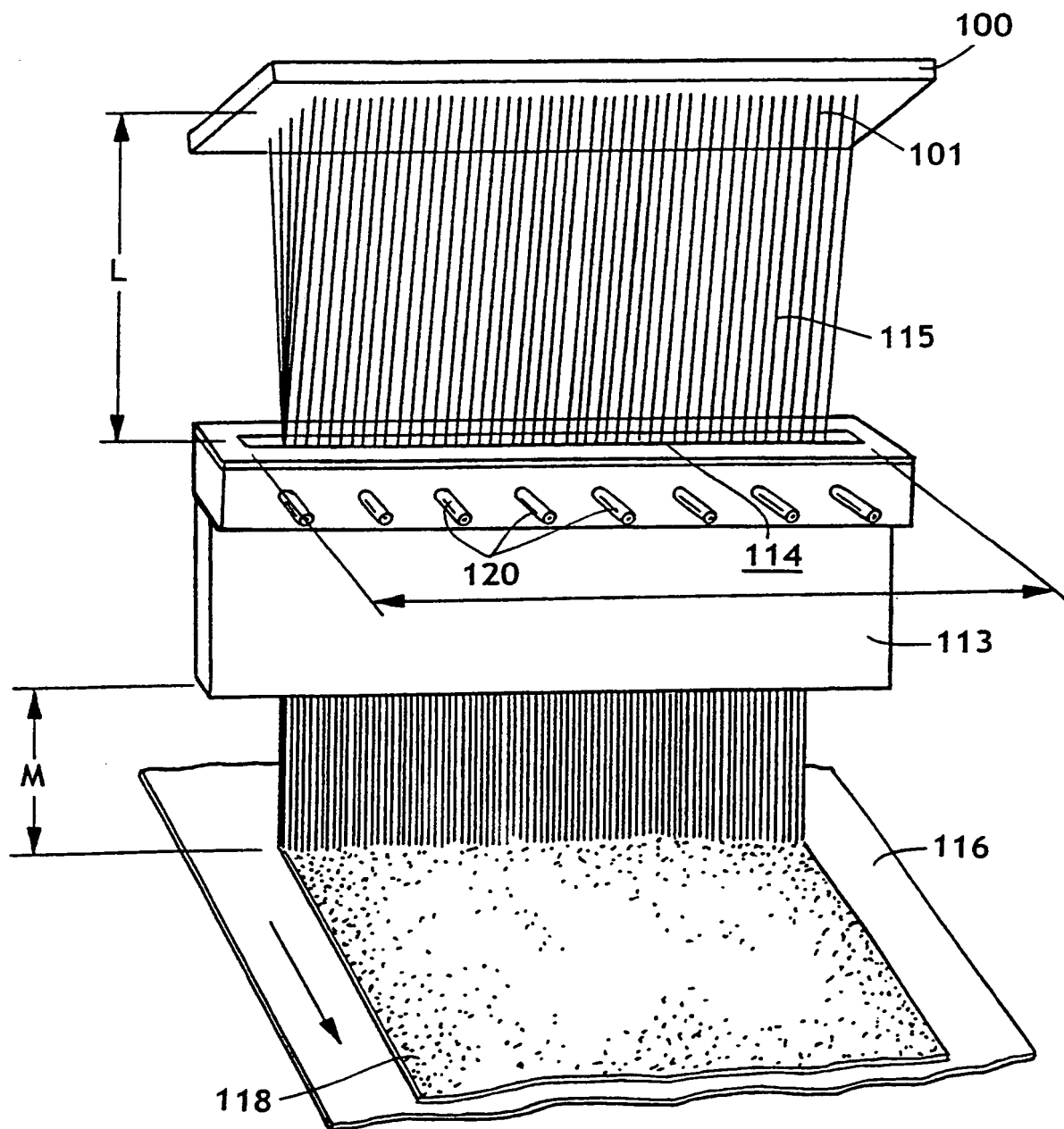


FIG. 10

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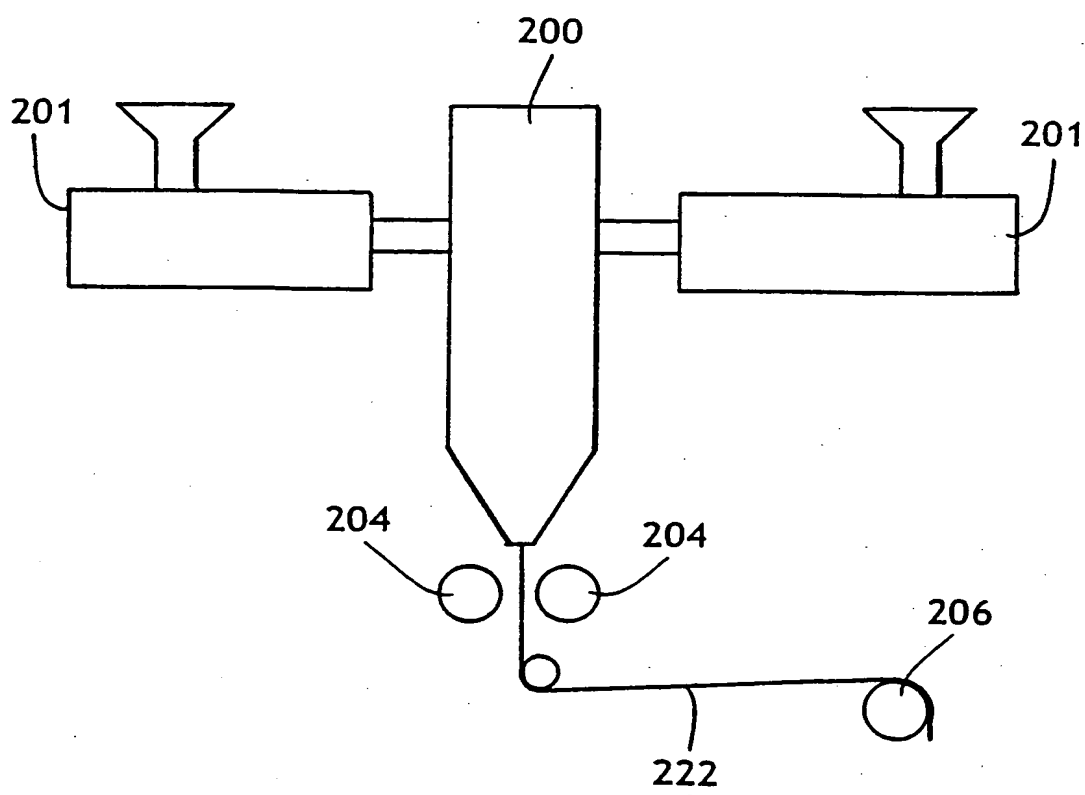


FIG. 11

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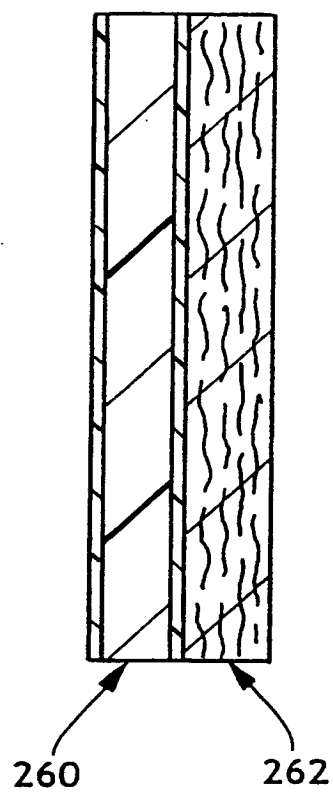


FIG. 12

## INTERNATIONAL SEARCH REPORT

national Application No

PCT/US 99/31277

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G18/12 C08G18/48 C08G18/83

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 0 773 315 A (FULLER H B LICENSING FINANC) 14 May 1997 (1997-05-14) page 3, line 3 - line 36 claims 1,2,8 examples 1-3	3,5,6
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

29 March 2000

Date of mailing of the international search report

06/04/2000

Name and mailing address of the ISA

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 99/31277

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 5 204 110 A (ALLAIRE MICHAEL J ET AL) 20 April 1993 (1993-04-20) example I	16-20

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Information on patent family members

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CORRECTED VERSION

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
6 July 2000 (06.07.2000)

PCT

(10) International Publication Number  
WO 00/039179 A1

(51) International Patent Classification<sup>7</sup>: C08G 18/12,  
18/48, 18/83

(21) International Application Number: PCT/US99/31277

(22) International Filing Date:  
30 December 1999 (30.12.1999)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/114,197 30 December 1998 (30.12.1998) US  
60/114,198 30 December 1998 (30.12.1998) US

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(81) Designated States (*national*): AE, AL, AM, AT, AU, AZ,  
BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK,  
DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL,  
IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU,  
LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT,  
RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA,  
UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent  
(AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent  
(AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU,  
MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM,  
GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

(48) Date of publication of this corrected version:  
4 December 2003

(15) Information about Correction:  
see PCT Gazette No. 49/2003 of 4 December 2003, Sec-  
tion II

For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: SUPERABSORBENT AND ELASTIC POLYMERIC MATERIAL INCLUDING POLYETHYLENE GLYCOL AND  
POLYTETRAMETHYLENE ETHER GLYCOL SOFT SEGMENTS AND METHODS OF MAKING SAME

(57) Abstract: A superabsorbent and elastomeric thermoplastic polymer includes soft segments and hard segments which contribute to the functionality of the polymer. The soft segments have a molecular weight in the range from about 600 to about 20,000 and are selected from the group of PEG, PEO, PTMEG, PPG and PPO. The hard segments are selected from the group of polyurethanes, polyamides, polyesters, polyureas, and combinations thereof. The soft and hard segments are covalently bound together by means of urethane, amide, ester or secondary urea linkages or combinations.

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